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ABSTRACTS OF CURRENT PUBLISHED INFORMATION ON NICKEL AND ITS ALLOYS

NICKEL

Refining of Nickel at the Clydach Plant of The Mond Nickel Co., Ltd.

'Twenty-five Years' Progress in Nickel Refining.'
Industrial Chemist, 1959, vol. 35, Dec., pp. 583–8.

The carbonyl process for the refining of nickel has been in operation since 1902, and it has remained basically unchanged until the present day. Briefly, the process depends on the reversible reaction between nickel and carbon monoxide: nickel carbonyl forms at 50°C. and subsequently decomposes at 200°C. As the carbonyl reaction is highly selective, nickel can be volatilized from the other metallic constituents and eventually recovered, in a high state of purity, by decomposition.

A comprehensive description of the Mond process, as it was then carried out at the Clydach Refinery of The Mond Nickel Company, Ltd., was published in *Industrial Chemist* in 1934. Since that time a great deal of effort has been expended in developing the process, and remarkable improvements in efficiency have been achieved. Not only has the throughput per plant unit been greatly increased (thus reducing the number of units required for a given output) but the thermal efficiency, i.e., the amount of producer gas required for the production of a unit of nickel, has been improved several-fold. While much of this increased efficiency has been the result of refinements in technique rather than of major changes in the process, an important advance was made recently when a new decomposer unit of radically new design was brought into operation by the Company. Other major changes have been the installation of a copper-liquor plant for gas separation, the introduction of pressure refining for the production of nickel and iron powders, and provision of new facilities for carbon-monoxide enrichment.

These developments are described in the present article. The review includes a flowsheet illustrating the extraction of nickel by the carbonyl process, and photographs of the new decomposer plant supplement the description given in the text.

Creep of Cold-Drawn Nickel

W. D. JENKINS and C. R. JOHNSON: 'Creep of Cold-Drawn Nickel.'
Jnl. Research, Nat. Bureau Standards, 1959, vol. 63C, July–Sept., pp. 1–18.

Creep tests were conducted in tension, under constant loads and at temperatures of 300°, 700°, 900° and 1200°F. (150°, 370°, 480° and 650°C.), on specimens of nickel initially cold-drawn to 40 per cent. reduction in area.

Because of their inadequacy in describing the changes in structure accompanying the creep processes, none of the equations proposed by other investigators for definition of the strain–time relationship was found suitable for expressing or predicting the creep-test results of the investigation with high accuracy. Conformance with the parabolic strain–time law was, however, obtained over limited ranges of stresses and strains.

The authors discuss the effects of cold-drawing on the creep properties. Certain etching techniques were employed that gave evidence of the presence and movement of dislocations in the structure.

Diffusion of Activator Elements in Oxide-Coated Cathode Nickel

H. MIZUNO: 'Doping Influences on Activator Diffusion in Oxide-Coated Cathode Nickel.'
Jnl. Physical Soc. Japan, 1959, vol. 14, Oct., pp. 1295–1301.

It is generally supposed that thermionic emission occurs in oxide-coated cathode nickel as a result of the diffusion of the activators in the basis nickel to the oxide-coating/nickel interface, where they react with the barium-oxide coating to yield free barium atoms. The rate of diffusion of the activators present in the nickel is therefore a factor of primary importance to the performance of the cathode. In previous studies of this factor little or no account has, however, been taken of the influence, on the diffusion rates of any one activator, of the other activators present. The work described was carried out in an attempt to obtain information in this connexion.

In each of the four cathode-nickel alloys studied, the content of one of the activator elements was controlled so as to determine its effect on the rate of diffusion of another. In this way the diffusion rate of magnesium was determined as a function of, respectively, the manganese, iron and silicon content, and that of manganese was studied in relation to the magnesium content. Particulars of the experimental procedure and the results obtained are given in the paper.

Consideration of these results leads the author to three main conclusions: (1) doping exerts a significant influence on the diffusion of activators in oxide-coated cathode nickel; (2) the diffusion coefficient of magnesium decreases as the manganese, iron or silicon content of the oxide-coated cathode is increased; (3) the diffusion coefficient of manganese increases with increase in the magnesium content of the cathode nickel.

Anodic Dissolution and Electrolytic Polishing of Nickel

J. K. HIGGINS: 'The Anodic Dissolution and Electrolytic Polishing of Metals.'

Jnl. Electrochemical Soc., 1959, vol. 106, Dec., pp. 999–1005.

Theories advanced in explanation of the anodic dissolution of metals under conditions associated with electrolytic polishing have been evolved mainly on the basis of data derived from studies of the anodic dissolution of copper in phosphoric acid. In some of these theories emphasis is placed on the rôle played by salt and oxide films during polishing, and the work now described was initiated to determine the validity of the theories when applied to the interpretation of the anodic behaviour and electrolytic polishing of other metals, in this case, nickel in hydrochloric acid.

The study was carried out using the potentiostat technique (by which the anode potential is maintained at any arbitrary value by control of the current) to obtain potential/current-density curves under various experimental conditions. As a means of investigating the relationship between electrolytic polishing and passivity, some tests were conducted to study the anodic dissolution of copper in potassium-cyanide solutions containing potassium hydroxide.

Full details of the experimental procedures employed, and of the data obtained, are given in the paper. The main findings of the investigation are summarized as follows:

'(1) The anodic dissolution of nickel in dilute ($<7N$) HCl solutions is diffusion-controlled.

'(2) At prepolarized anodes in concentrated ($>7N$) solutions, the dissolution is diffusion-controlled.

'(3) At non-prepolarized anodes in concentrated ($>7N$) HCl solutions the simple diffusion mechanism breaks down.

'(4) The onset of thick salt-film formation in the more concentrated ($>7N$ HCl) solutions is associated with a decrease in the degree of hydration of the dissolving salt.

'(5) The state of the prepolarized anode is unstable; it reverts to the non-prepolarized condition in a short time.

'(6) Polishing in the dilute solutions can be explained satisfactorily by the differential solution of peaks and cavities due to different concentration gradients at peaks and cavities and the deposition of freely-soluble salt films.

'(7) The brightening effect observed under very thick salt films in concentrated acid solutions is best explained by the dissolving-oxide theory of polishing.

'(8) Passivity can be induced gradually in a polishing bath by increasing the alkalinity of the electrolyte in steps, and this supports the theory mentioned in (7).'

Chemisorption of Carbon Monoxide and Oxygen on Nickel Films

R. SUHRMANN, G. WEDLER and H. HEYNE: 'Electron Affinity and Kinetics during Chemisorption of Carbon Monoxide and Oxygen on Nickel Films.'

Zeitsch. physikalische Chemie, 1959, vol. 22, Dec., pp. 336–58.

A study was made of the influence of carbon monoxide or oxygen on nickel films, 40–85 Å thick, vacuum-deposited in an ultra-high-vacuum apparatus. Variations in electrical resistivity were recorded and the pressure and the amount of gas adsorbed were determined.

It was found that the spontaneous and time-dependent increase in the resistivity observed during chemisorption of carbon monoxide could, at the beginning of the first addition, be described in terms of a superimposition of a first-order reaction on a second-order reaction. As coverage continued, the resistivity increased in accordance with a first-order reaction. In both cases the kinetics of the reaction could be depicted also by the Elovich equation.

Little change in resistivity occurred after a coverage $\theta=0{\cdot}5$ CO molecules per surface nickel atom, although further molecules were irreversibly chemisorbed. This behaviour is taken to indicate that chemisorption was initially preponderantly through two nickel atoms, and then, from $\theta=0{\cdot}5$, through one nickel atom. Support for this interpretation is found in the fact that metal-electron affinity per CO molecule is initially two and then one.

During chemisorption of oxygen the spontaneous increase in resistance continued beyond monoatomic coverage. A time-dependence effect was observed only from $\theta\approx 1$ and was described by superimposition of a first-order reaction on a second-order reaction, or by means of the Elovich equation. The electron affinity during oxygen chemisorption comprises two metal electrons per oxygen atom.

Reduction of Nickel Oxide

R. E. CECH: 'The Reduction of Nickel Oxide.'

Trans. Metallurgical Soc., Amer. Inst. Mining, Metallurgical and Petroleum Engineers, 1959, vol. 215, Oct., pp. 769–81.

The process of reduction of oxide to metal is one of considerable complexity, involving a chemical reduction reaction, mass transport of reducing agent to, and reaction product away from, the point of reaction, and finally a transformation whereby metal atoms released from the oxide rearrange to form a stable reduced phase. Moreover, nucleation of the reduced phase affects the overall reaction kinetics. Previous investigations in this field have been concerned mainly with the thermodynamic aspects of reduction. The investigation now described was carried out, using metallographic and X-ray techniques, to gain information on: sites for nucleation of the reduced phase on nickel-oxide single crystals; the orientation relationships between the reduced metal and the parent oxide; and the metal-atom rearrangement following

reduction. Complementary studies were made of the initial-growth characteristics of nickel crystals on nickel oxide.

The single crystals of nickel oxide, which were prepared by reacting nickel bromide and water vapour (at 650°C. and a pressure of 25 mm. of mercury) on cleaved surfaces of magnesium-oxide single crystals, were reduced (in contact with a reducing gas consisting of hydrogen, water vapour and argon) immediately after their formation. The relationships between the orientation of the reduced nickel and the parent oxide (discussion of relevant data showing that these relationships are well defined takes up a large section of the paper) were inferred from the orientations exhibited by nickel foil produced by complete reduction of cube-oriented single-crystal sheets of nickel oxide. The tentative conclusions drawn with respect to metal-atom rearrangement are based on the metal/oxide relationships and the effect, on these relationships, of the reduction temperature.

The data indicate that reduction begins at points where structural singularities in the oxide intersect the surface. After nucleation of metal crystals, a thin film of nickel grows from the nuclei and completely covers the oxide-crystal surface. The observations on the structure of completely-reduced crystals suggest that the later stages of reduction may be accomplished by a reaction occurring primarily around the line singularities observed at the time of nucleation.

The fully-reduced structure, consisting of nickel having finely-dispersed worm-like voids, has a large surface area per unit volume of metal. It is considered possible that this type of structure contributes to the catalytic activity usually encountered in nickel reduced from the oxide.

Reaction of Nickel Carbonyl with Cyclopentadiene

O. E. FISCHER and H. WERNER: 'Dicyclopentadiene-nickel (0).

Chemische Berichte, 1959, vol. 92, June, pp. 1423-7.

It has been known for some time that, besides the pure cyclopentadienyl-metal complexes (ferrocene prototype), there exist complexes of mixed type, such as $C_5H_5RhC_5H_6$ or $C_5H_5IrC_5H_6$. Prior to the work described, however, the existence of pure C_5H_6-π complex of $Me(C_5H_6)_2$ type had not been established.

Nickel carbonyl was transformed, under reflux conditions and using solvents such as benzene, ether or hexane, to give readily-volatile, dark-red dicyclopentadiene-nickel (0), $Ni(C_5H_6)_2$, in accordance with the following reaction:

$$Ni(CO)_4+2C_5H_6 \rightarrow Ni(C_5H_6)_2+4CO$$

The air-sensitive, diamagnetic complex, which is monomerically soluble in organic solvents, is the first evidence that Ni(0) can be stabilized through four π-bonds even with two 'diene' groups. A sp^3-hybridization of the metal with tetrahedral co-ordinative co-valences is postulated.

In a similar manner $Ni(C_5H_5CH_3)_2$ can be obtained by interaction of nickel carbonyl and methyl-cyclopentadiene in n-hexane.

Reactions of Carbon Monoxide: the Function of Nickel Carbonyl in a New Synthesis

G. P. CHIUSOLI: 'Reactions of Carbon Monoxide: the Function of Nickel Carbonyl in a New Synthesis.'

Gazzetta Chimica Italiana, 1959, vol. 89, May-June, pp, 1332-37.

A description is given of new syntheses of carboxylic acid and esters from the chlorinated derivatives of allyl compounds and carbon monoxide catalyzed with nickel carbonyl. These syntheses are compared, on the one hand, with the reaction of dimerization of the chlorinated derivatives of allyl compounds and, on the other, with the carboxylation of acetylene to acrylic acid or acrylic esters. A scheme is proposed in which the basic mechanism is considered to be the primary formation of a complex of a co-ordination compound derived from the reaction between nickel carbonyl and the chlorinated derivative.

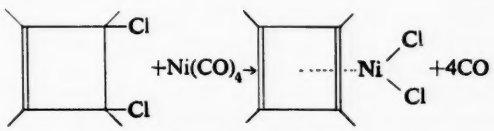
A Nickel-Chloride Adduct of Tetramethyl-cyclobutadiene

R. CRIEGEE and G. SCHRÖDER: 'A Derivative of Cyclobutadiene.'

Annal. Chemie, 1959, vol. 623, pp. 1-8.

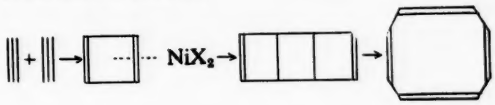
Over the past 50 years attempts have been made, without success, to prepare, or at least to obtain proof of the existence of, this interesting cyclobutadiene. On the basis of theoretical considerations, it was postulated that, in the form of its nickel complex ($C_4H_4NiX_2$), the compound would be stable. Complexes of similar type were also postulated as intermediates in the Reppe synthesis of cyclooctatetraene from acetylene.

Work in this connexion has now resulted in determination of a complex of the relevant type, produced by transformation of nickel carbonyl with tetramethyl-dichlor-cyclobutene, in solvents such as benzene, acetone or ether, according to the following reaction:



The compound was obtained in the form of a reddish-violet crystalline powder which is soluble in water and in various organic solvents. The complex is diamagnetic (corresponding to a dsp^2 configuration of the nickel). Analytical, spectroscopic and nuclear-resonance studies showed the complex to be a true derivative of cyclobutadiene, the dimer of which was formed through thermal decomposition.

The findings of the present work reinforce the hypothesis that the Reppe synthesis of cyclooctatetraene progresses as follows:



Crystal Structure of $Ni_{12}P_5$

S. RUNDQVIST and E. LARSSON: 'The Crystal Structure of $Ni_{12}P_5$.'

Acta Chemica Scandinavica, 1959, vol. 13, No. 3, pp. 551–60.

The investigation of the Ni–P system of which the study reported formed a part was initiated to supplement the relatively little information available on the nickel phosphides, to establish the existence and compositions of the intermediate phases, and to determine crystal structures. The section of the investigation described was concerned with determination of the crystal structure of $Ni_{12}P_5$, a phase not previously characterized.

The unit cell, containing two formula units, was found to be tetragonal: $a=8{\cdot}646$ Å; $c=5{\cdot}070$Å. The space group is $I4/m$-(C_{4h}^5) with 16 Ni in 16(*i*): $x=0{\cdot}116_0$; $y=0{\cdot}182_2$; $z=0{\cdot}248$; 8 Ni in 8(*h*): $x=0{\cdot}368$; $y=0{\cdot}060$; 8 P in 8(*h*): $x=0{\cdot}195$; $y=0{\cdot}415$; and 2 P in 2(*a*). $Ni_{12}P_5$ is compared with related structures and some phase-analytical observations on the Ni–P system are reported. NiP_3 is cubic, $a=7{\cdot}819$ Å; and isostructural with CoP_3, $a=7{\cdot}706$ Å. Both NiP_3 and CoP_3 belong to the *D*2 ($CoAs_3$) structure type.

Influence of Metal Content on the Properties of Spores

R. SLEPECKY and J. W. FOSTER: 'Alterations in Metal Content of Spores of *Bacillus Megaterium* and the Effect on Some Spore Properties.'

Jnl. Bacteriology, 1959, vol. 78, July, pp. 117–23.

The relation of metal ions to bacterial spores has been studied almost invariably from the standpoint of the influence of their presence, during bacterial growth, upon the degree of subsequent sporulation of the cultures. Information on the participation of metal ions in the sporulation process, and on their incorporation in spores, relates mainly to calcium, and originated in the discovery, by CURRAN *et al.*, of the high concentration of calcium in the spores of various *aerobic bacilli* as compared to the vegetative cells. In subsequent work the question arose as to whether calcium enrichment is requisite (*a*) for formation of a spore, and (*b*) for resistance of the spore to various imposed stresses. The investigation now described was intended to throw light on these problems by determination of the change in metal-cation content of spores of *Bacillus megaterium* with change in the metal content of the medium.

Spores were harvested from a chemically-defined liquid medium containing individual trace additions (at levels comprising the maximum and minimum concentrations ensuring essentially complete sporulation of the culture) of the following elements: calcium, zinc, nickel, copper, cobalt and manganese. The various crops of washed spores were analysed to determine the amount of metal (and also of calcium) present. A study was made of (1) the influence of the metal content of the medium on the metal content of the spores; (2) the influence of other metals present in the medium on the calcium content of the spores; and (3) the properties (thermal resistance, resistance to ultraviolet irradiation, resistance to dessication, and resistance to phenol) exhibited by spores with various metal contents.

The results show that the content of the individual metals in the spores varied over a very wide range and was governed by the concentration of the particular metal in the growth medium. Accumulation of calcium and nickel was particularly striking, and accumulation of zinc and manganese was also pronounced. The accumulation of the other metals studied appeared to be accompanied by a reduction in the amount of calcium taken up, and the various cations present in spores seem therefore to be to a certain extent interchangeable. The spores containing maximal and minimal amounts of metal did not differ in morphology, staining characteristics, refractility, and resistance to dessication, phenol and ultraviolet irradiation. Calcium appeared to be a prerequisite for achievement of high thermal resistance.

Determination of Nickel in Zirconium

U.K. ATOMIC ENERGY AUTHORITY: 'Analytical Method for the Absorptiometric Determination of Nickel in Zirconium Metal.'

U.K. Atomic Energy Authority, Production Group Report 22(*S*), 1959; 5 pp. Price 1/3.

The report describes a procedure suitable for determination of trace amounts of nickel (5–60 p.p.m.) in zirconium.

The technique, which is stated to be accurate to $\pm 2{\cdot}4$ μg. at a nickel level of 40 μg., involves dissolving the zirconium sample in a mixture of hydrochloric acid and ammonium fluoride. Ammonium citrate is then added to complex the zirconium, and the pH of the solution is adjusted to approximately 8. The nickel is extracted into chloroform as its dimethylglyoxime complex, and then back extracted from the chloroform with dilute hydrochloric acid. The metal is finally determined absorptiometrically as its oxidized dimethylgloxime complex, using the Spekker absorptiometer.

It is emphasized that, due to the explosive properties of zirconium, safety precautions must be taken before commencing work.

ELECTRODEPOSITION AND OTHER COATING METHODS

Corrosion-Resistance of Nickel Coatings Deposited by 'Kanigen' Plating

J. R. SPRAUL: 'Corrosion Data for Chemical Nicke Plating.'

Plating, 1959, vol. 46, Dec., pp. 1364-9.

In the few years since electroless nickel plating was first introduced on a commercial scale, the range of applications found by the process has extended considerably. The purpose of this paper is to present data

illustrating the resistance of such deposits to a wide range of corrosive media.

Full particulars are given of the pre-treatment procedures used to prepare the carbon-steel test panels for plating. In outlining the composition of the 'Kanigen' plating solution and the plating conditions used in the investigation, the author makes the comment that 'while this plating solution is not the most efficient for all types of base material, nor the fastest, it represents a practical compromise between universality, quality of deposits and economy'. The phosphorus contents of the coatings ranged from 7 to 10 per cent. Some of the deposits were heat-treated before testing.

Data are tabulated on the resistance of the coatings to corrosion by more than sixty media. Chemical nickel plating has proved particularly suitable for applications in which contamination and discoloration of the commodity by iron cannot be tolerated, i.e., in which the rate of corrosion of the deposit is less than 0·1 mil/year. Of the corrosive media studied, the following attacked the nickel coatings at a rate less than this value:

Acetone	Ethylene glycol
Acetylene bromide	Gasoline
Acrylonitrile	Isoamyl octyl orthophosphate
Allyl chloride	Methyl alcohol
Amyl acetate	Naphtha
Amyl alcohol	Oleic Acid
Beer	Petroleum white oil
Benzol	Photographic developer
Benzyl acetate	Photographic hypo
Benzyl alcohol	Resin (amine)
Black liquor skimmings	Resin (polyester)
Caprolactam monomer	Resin (alkyd)
Carbon disulphide	Rosin Size
Carbon tetrachloride	Sodium carbonate, 10%
Cetyl alcohol	Sodium hydroxide
Cobalt linoleate	Sugar, liquid
Cresylic acid	Tall oil, crude,
Dibutyl phthalate	Tall oil, refined
Diphenyl	Urea solutions
Ethyl alcohol	Water, deionized

In other tests, steel and aluminium-alloy panels chemically plated with nickel were exposed to a 'mild salt, humid, industrial atmosphere' to determine the effects, on corrosion-resistance, of variations in pre-treatment, coating thickness, basis material, surface roughness and post-plating treatments. Commenting briefly on the salient findings, the author refers to the differences in the corrosion behaviour of electro-deposited and chemically-deposited nickel coatings and to the fact that surface roughness contributes to failure. Optimum atmospheric-corrosion-resistance was conferred on chemically plated steel when the component was heat-treated for four hours at 1400°F. (760°C.) and the basis steel subjected to pre-treatment in a high-temperature molten-salt bath. A coating thickness greater than 2 mils is required to limit rusting to 0·25–0·5 per cent. of the surface over periods longer than 12 months.

Various aluminium alloys with nickel coatings at least 2 mils thick were subjected to three years' exposure without significant failure. The optimum pre-treatment cycle comprised vapour degreasing, cleaning with dilute sodium-hydroxide/sodium-nitrite solution, a ferric-chloride/hydrochloric-acid pickle, and a bright dip in a hydrofluoric-acid/nitric-acid solution.

Electrodeposition of Molybdenum Alloys: Literature Review

J. Z. BRIGGS and H. W. SCHULTZE: 'A Literature Review on the Use of Molybdenum as an Alloy in Electrodeposits.'

Plating, 1959, vol. 46, Dec., pp. 1370-6.

Iron, cobalt and nickel appear to be the only elements that permit co-deposition of substantial amounts of molybdenum (in some cases as high as 50–60 per cent.) Molybdenum does not co-deposit with tungsten alone, although both metals can be deposited together in ternary alloys. Alloys of molybdenum with some other metals can be deposited from certain solutions, but very high current densities are required and the current efficiency may be very low: the amount of molybdenum in the deposits is often so small as to raise the question as to whether the metal is really present as an alloy, or merely adsorbed on the surface or occluded as a salt.

The presence of about 10 per cent. of molybdenum has been reported to increase the wear-resistance of hard chromium deposits three to eight times, while, in other alloys, molybdenum appears to have a beneficial effect not only on corrosion- and wear-resistance, but also on hot-hardness and magnetic and electrical properties. The present survey was conducted to review the literature on electrodeposition of molybdenum-containing alloys and on the properties of the deposits (reference is made to a *bibliography* of 55 items).

Information on electrodeposition of the following systems is discussed: chromium-molybdenum, cobalt-molybdenum, copper-molybdenum, gold-molybdenum, iron-molybdenum, nickel-molybdenum, zinc-molybdenum, cobalt-chromium-molybdenum, cobalt-molybdenum-tungsten, copper-zinc-molybdenum, nickel-iron-molybdenum, nickel-iron-molybdenum-copper and nickel-iron-molybdenum-manganese.

NON-FERROUS ALLOYS

Specification Requirements for Gunmetal Castings

F. HUDSON and E. C. MANTLE: 'Specification Requirements for Gunmetal Castings.'

Foundry Trade Jnl., 1960, vol. 108, Jan. 21, pp. 69-76; disc., pp. 76-80.

These two papers, presented at a meeting of the London Branch of the Institute of British Foundrymen, Autumn 1959, deal with a subject, gunmetal specifications, which is of particular interest in view of the controversy aroused among founders and ingot

manufacturers by the proposed revision of B.S. 1400 (covering copper-base castings).

The paper by F. HUDSON (pp. 69–73) opens with a discussion of data indicating that the production of copper-base alloy castings in the U.K. is not keeping pace either with the growth in population or increase in the production index; in the U.S.A. output of such castings has even declined since 1946. The author suggests that this trend can be reversed only by (a) research to discover new applications, (b) improvements in quality, (c) stabilizing prices, and (d) intensifying sales efforts. The first of these two points, and the relation they bear to specifications for gunmetal castings, are dealt with in the present paper.

The wisdom of introducing impurity limits into B.S.1400 is considered, and the advantages of standardizing on a minimum number of alloys are emphasized. In the author's opinion, standardization on three grades of leaded gunmetal with a similar basis composition, e.g., LG1 (83-3-9-5), LG2 (85-5-5-5), and a slightly-modified form of LG3 (87-7-4-2), would be of great benefit to the industry as a whole.

The paper includes a brief outline of work, carried out by The Mond Nickel Company, Ltd., which has demonstrated that the use of a leaded gunmetal containing about 6½ per cent. tin, 3 per cent. zinc, 3½ per cent. lead, 2 per cent. nickel, remainder copper, renders possible the production of castings, of variable section, combining excellent mechanical properties (similar to those obtainable in 88-10-2 gunmetal) with the castability and pressure-tightness normally associated with 85-5-5-5 gunmetal. (See, in this connexion, also abstract in *Nickel Bulletin*, 1959, vol. 32, No. 12, p. 356.)

In the second paper (pp. 73–6) E. C. MANTLE gives a brief account of three research programmes (in progress at the British Non-Ferrous Metals Research Association) which have some bearing on gunmetal specifications:

(1) To determine the gunmetal composition giving minimum porosity, a study was made of the influence of the major alloying elements on the properties of existing gunmetals. Data on pressure-tightness, tensile properties of test bars and castings, and creep-resistance at 232° and 288°C. are presented for gunmetals of G1, LG2 and LG3 grade, and also for 'B.N.F. Gunmetal' (copper 87½, tin 7½, zinc 2, lead 3, per cent.) which appeared to offer a better combination of properties than any of the other alloys.

(2) Some findings of an investigation of the influence of impurities on the properties of gunmetal castings are presented.

(3) An outline is given of work which resulted in the evolution of a test bar which, using a reasonably high-casting temperature, and pouring as rapidly as possible, gives very consistent results.

Copper-Nickel-Tantalum Heat-Resisting Alloys

See abstract on p. 56.

Diffusion in the Nickel-Uranium System

N. MÜLLER: 'Studies of Diffusion in the Uranium-Zirconium and Nickel-Uranium Systems.'

Zeitsch.f. Metallkunde, 1959, vol. 50, Nov., pp. 652–60.

Diffusion in the uranium-zirconium system was studied at temperatures higher than the transformation temperature of the γ phase; that in the nickel-uranium system was investigated over the range 300°–700°C. The data are presented and discussed *in extenso*.

All the intermediate phases indicated in the equilibrium diagram occurred in the uranium-nickel system during diffusion. In both systems a Kirkendall Effect was observed, a finding on the basis of which it is suggested that the diffusion process occurs by a vacancy mechanism.

Study of the Nickel-Indium-Carbon System

L. J. HÜTTER, H. H. STADELMAIER and A. C. FRAKER: 'The Ternary System Nickel-Indium-Carbon.'

Metall, 1960, vol. 14, Jan., pp. 21–2.

Details are given of a study of the nickel-rich corner of the ternary system nickel-indium-carbon. The alloys, containing up to 32 at. per cent. of indium, were examined by microscopical and X-ray techniques, supplemented, in some cases, by determination of cooling curves.

In the region investigated the following phases were determined: nickel solid solution; graphite; the binary compounds Ni_3In and ε-Ni_2In; and the ternary carbide Ni_3InC. The reactions involved are discussed in the light of the phase diagrams developed and by reference to photomicrographs.

Determination of Cobalt in Nickel Alloys

See abstract on p. 63.

NICKEL-IRON ALLOYS

$\gamma \rightleftharpoons \alpha$ Transformation in Iron-Nickel Alloys

E. SCHEIL and W. NORMANN: 'Investigation of Thermodynamic Parameters in the Martensitic $\gamma \rightleftharpoons \alpha$ Transformation in Iron-Nickel Alloys.'

Archiv f.d. Eisenhüttenwesen, 1959, vol. 30, Dec., pp. 751–4.

Although the iron-nickel alloys have long been used as representative materials for study of the martensitic transformation, information on the thermodynamic parameters of the system is incomplete. Data on the difference between the thermodynamic potentials of the α and γ phases at the temperature of the martensitic transformation are of particular significance in this respect.

In the investigation described the enthalpy of a series of iron-nickel alloys containing 0–25 per cent. nickel were determined over the range 20–900°C., using calorimetric techniques. From the curves obtained the heats of transformation at the $\alpha \rightleftharpoons \gamma$ transformation were determined, and these then enabled

calculation of the differences in the thermodynamic potentials (free enthalpy).

Details are given also of an apparatus by means of which the influence of hydrostatic pressure on the temperature of transformation was studied.

Stabilization of the Martensitic Transformation in Iron-Nickel Alloys

J. WOODILLA, P. G. WINCHELL and M. COHEN: 'Stabilization of the Martensitic Transformation in Iron-Nickel Alloys.'

Trans. Metallurgical Soc., Amer. Inst. Mining, Metallurgical and Petroleum Engineers, 1959, vol. 215, Oct., pp. 849–51.

Although previous workers have shown that interstitial elements play an important rôle in the stabilization of martensitic transformations in iron-base alloys, investigations of the temperature-dependence of the stabilization process have given rise to values (~11,000 cal./mol.) that are not readily identifiable with the activation energy for diffusion of carbon (or nitrogen) in either ferrite or austenite. In the work reported, the isothermal mode of the martensitic reaction was employed to derive the activation energy for stabilization.

The experiments were carried out on specimens of an iron-nickel alloy (containing 30·8 wt. per cent. of nickel and 0.007 wt. per cent. of carbon) some of which were decarburized and denitrogenized before austenization and water-quenching. The isothermal martensitic transformation was followed by determination of changes in electrical resistance.

Although the carbon (or nitrogen) content may be very low in the alloys studied, it is considered, on the basis of the results reported, to play an important rôle in the stabilization phenomenon: when these interstitial elements were removed by moist-hydrogen treatment, no evidence of stabilization was found. At a carbon content of 0·007 wt. per cent., the activation energy for the stabilization process was comparable to that for the diffusion of carbon (or nitrogen) in ferrite rather than in austenite, a finding which suggests that the interstitial diffusion controlling the stabilization process occurs within the martensitic embryos rather than in the matrix of the parent phase. The kinetics data further indicate that the interstitial atoms tend to diffuse from the embryos towards the surrounding regions, thereby immobilizing the interface, and this reaction appears to be the origin of the stabilizing effect observed in the alloys.

Influence of Neutron Irradiation on the Martensitic Transformation in Iron-Nickel Alloys

L. F. PORTER and G. J. DIENES: 'Effect of Neutron Irradiation on the Martensite Transformation in Iron-Nickel Alloys.'

Trans. Metallurgical Soc., Amer. Inst. Mining, Metallurgical and Petroleum Engineers, 1959, vol. 215, Oct., pp. 854–63.

Considerable evidence is available indicating that neutron irradiation is capable of influencing phase changes in metals and alloys, although the mechanism of the effect is often not well understood. Work in this connexion might well throw light not only on irradiation damage but also on the phase changes involved. In this paper the authors give details of an investigation of the effects of neutron irradiation on the martensitic transformation in iron-nickel alloys containing 26·37, 28·9 and 30·4 wt. per cent. of nickel. The M_s temperature was determined, and the course of transformation studied, by measuring electrical resistance, as a function of temperature, while the specimens were being cooled at a constant rate of 3–4C.°/minute.

The data presented demonstrate that formation of martensite was retarded by neutron irradiation, the degree of retardation increasing with time of exposure and being more severe when the alloy was treated to produce a coarse-grain matrix structure. This effect is thought to be associated with an increase in the critical shear stress of the matrix material as a result of the radiation damage remaining after exposure.

During irradiation, changes in electrical resistance and magnetic saturation induction occurred which are ascribed to the separation of phases or to the formation of nickel-rich clusters due to radiation-enhanced diffusion.

In specimens partially transformed to martensite, recovery of the plastic deformation produced by such prior transformation was observed in both the control and irradiated specimens, though the extent of such recovery in the presence of the radiation field was about double that observed, as a result of thermal treatment, in the control specimens. Possible mechanisms accounting for the radiation effects observed are discussed.

CAST IRON

Hardenability of S.G. Iron

J. GITTUS: 'The Hardenability of Spheroidal Graphite Cast Iron.'

Iron and Steel, 1959, vol. 32, Dec., pp. 559–65.

Most S.G. iron castings have hitherto been used in the pearlitic or ferritic (annealed) condition, but attention is now being focused on their use in the quenched-and-tempered condition, the production of which necessitates information on the hardenability of the material. A survey of the literature indicated that in the more comprehensive and authoritative of the previous investigations use had been made of the Jominy end-quench tests as a criterion of the hardenability of S.G. iron, and, in the initial stages of the present study, the same method was employed to assess the effects, on hardenability, of the presence of silicon, manganese and nickel. Subsequently the deficiencies of this approach were realized, and it was decided to attempt to measure hardenability in terms of the uniformity, with change in section thickness, of the mechanical properties of quenched-and-tempered castings.

Having established a method of producing sound wedges, sixteen wedge specimens were cast, representing all the possible combinations covered by a simultaneous study, at two levels each, of the elements manganese, nickel, molybdenum and chromium (nominal contents: manganese 0·5 and 1·5, nickel 1 and 2, molybdenum 0 and 0·4, chromium 0 and 0·4, per cent.). The compositions of the sixteen specimens are given in the table below. Information on the structure of the various irons in the as-cast condition was obtained from metallographic examination of bars cast from the same heats as the wedges. Specimens from these bars were used also to establish the response of the different heats to tempering, and the data so obtained were then employed as a basis for development of tempering treatments which would, in all cases, produce the same hardness (about 360 Brinell at the tip of the wedge) when applied to fully martensitic castings. Impact and tensile tests were carried out on specimens obtained from various locations in the quenched-and-tempered wedges.

A number of combinations of the four alloying elements studied were found to increase the hardenability of S.G. iron. The most hardenable compositions appeared to be those numbered (7), (8), (12), (9), (13), (14) and (16) in the table below. Proof ratios did not vary significantly and were in the region of 0·9, but compositions (8), (13) and (14) exhibited the highest impact strengths. Composition (13) is considered the most satisfactory for castings up to 4 in. (10 cm.) thick since, unlike many other irons containing combinations of alloying elements, castings of this composition have no tendency to contain eutectic carbides. In cases where alloying elements promoted carbide formation, prolonged heat-treatments were found necessary to remove this undesirable, embrittling constituent.

Molybdenum, commonly specified as an alloying element for S.G. iron, was found to offer no special advantage, whether alone or in combination with other elements. Chromium, at least in the amounts studied, appeared to be deleterious; it did not improve hardenability, as defined in the paper, and it promoted formation of undesirable carbide constituents.

Welding of S.G. Iron

G. R. PEASE: 'The Welding of Ductile Iron.' *Welding Jnl.*, 1960, vol. 39, Jan., pp. 1s-9s.

In this critical review of information available on the welding of S.G. iron the author outlines the present state of progress in the field, comments upon the problems involved, and suggests approaches which might provide successful solutions to these problems.

The review opens with a résumé of the salient characteristics of the different grades of S.G. iron available. A discussion of the criteria and tests variously proposed as a means of assessing the weldability of the

Composition of S.G. Iron Wedge Specimens

(*See abstract on p. 47*)

Melt No.	Si %	Mg %	Ni %	Mn %	Cr %	Mo %
(1)	1·90	0·068	1·00	0·18	0·096	<0·10
(2)	1·90	0·062	1·00	0·21	0·096	0·59
(3)	2·05	0·096	1·35	0·22	0·59	<0·10
(4)	1·90	0·069	0·90	0·19	0·56	0·65
(5)	1·90	0·074	2·10	0·21	0·12	<0·10
(6)	1·85	0·090	2·00	0·40	0·010	0·86
(7)	1·80	0·069	2·10	0·41	0·36	<0·10
(8)	2·10	0·059	1·85	0·44	0·36	0·49
(9)	2·05	0·048	1·10	1·40	0·01	<0·10
(10)	2·05	0·051	1·05	1·30	0·01	0·60
(11)	2·05	0·067	1·00	1·40	0·50	<0·10
(12)	2·20	0·073	0·99	1·35	0·44	0·65
(13)	2·05	0·064	1·90	1·40	0·01	<0·10
(14)	2·20	0·078	2·20	1·40	0·051	0·40
(15)	2·20	0·073	2·20	1·40	0·67	<0·10
(16)	2·20	0·054	2·15	1·40	0·57	0·45

material is followed by a survey of the problems presented by the hard structures associated (with the exception of the austenitic grades) with the heat-affected zone of fusion-welded S.G. iron. Subsequent sections are concerned with casting defects, the properties of welded joints produced using various welding techniques and electrodes, and the welding of S.G. iron to dissimilar metals.

The points arising from the review are summarized by the author as follows:

'Strong, ductile joints are attainable in ductile iron, the best of which have properties which match, or nearly match, those of the 60-45-10 grade of casting. In most cases, however, long post-weld heat-treatments are required to attain these properties. As-welded joints are strong, but contain hard structures in the heat-affected zone which impair machinability, impact-strength and ductility.

'For any given set of welding conditions, or heat-treatment, there is a disturbing lack of reproducibility of results.

'Preheats of about 600°F. (315°C.) are highly desirable as a precautionary measure to prevent cracking, but, otherwise, have relatively little effect on the joint properties.

'For most applications, particularly those involving finished or semi-finished castings, the best results are obtained by metal-arc welding using covered electrodes of the ENiFe type. The casting should be low in phosphorus and alloy content, and, preferably, welded in the annealed condition. In common with other compositions, ductile-iron castings must be adequately prepared for welding by removing dross, shrinks, sponginess and other defects, if optimum-quality weldments are to be obtained.

'Where distortion is not a problem, good results can be obtained by using the oxyacetylene welding process and a cerium-containing ductile-iron filler rod.

'The need is indicated for more research effort in the following areas:

'1. Elimination of the hard (carbidic) heat-affected zone.

'2. Better reproducibility of results.

'3. Development of low-cost (preferably automatic) welding methods.'

CONSTRUCTIONAL STEELS

Low-Temperature Properties of Nickel-containing Materials

R. L. McGEE, J. E. CAMPBELL, R. L. CARLSON and G. K. MANNING: 'How Low Temperatures Affect Nine High-Strength Alloys.'

Materials in Design Engineering, 1959, vol. 50, Nov., pp. 106-7.

The article summarizes the salient data derived from tests carried out to determine, at 79°, —108°, —320° and —423°F. (26°, —78°, —196 and —253°C.), the tensile properties of the following nine structural materials used in aeronautical applications: '17-7 P.H.' and 'AM-350' precipitation-hardening steels; A.I.S.I. 4340 low-alloy nickel-chromium-molybdenum steel; 'Tricent' nickel-chromium-molybdenum-silicon steel; three titanium alloys; an aluminium alloy; and a magnesium alloy.

The authors' findings have been presented *in extenso* in *Wright Air Development Center Tech. Report* 58-386: see abstract in *Nickel Bulletin*, 1959, vol. 32, No. 9-10, p. 287.

Influence of Sulphur on the Notch-Toughness of Nickel-Chromium-Molybdenum Steels

J. M. HODGE, R. H. FRAZIER and F. W. BOULGER: 'The Effects of Sulphur on the Notch-Toughness of Heat-Treated Steels.'

Trans. Metallurgical Soc., Amer. Inst. Mining, Metallurgical and Petroleum Engineers, 1959, vol. 215, Oct., pp. 745-53.

Although it is generally recognized that, for applications in which notch-toughness is critical, the sulphur content of steels should be maintained at a low value, quantitative data on the influence of sulphur on notch-toughness has not so far been available. In many cases, particularly in flat-rolled products, impact properties are specified in the direction transverse to the principal rolling direction, so that the factors affecting the anisotropy or directionality of impact properties are also of concern to the stee producer. This paper gives details of an investigation conducted, at Battelle Memorial Institute, with the aim of obtaining quantitative information on the influence of sulphur content on notch-toughness of, and on the factors affecting the anisotropy of impact properties in, wrought heat-treated alloy steels.

The experimental steels studied, prepared from 600-lb. induction-furnace melts, were of the following nominal composition: carbon 0·3, silicon 0·25, manganese 0·8, nickel 2·5, chromium 0·8, molybdenum 0·45, per cent. Their sulphur contents were varied from 0·005 to 0·179 per cent. The ingots were rolled to 1·9-in. slabs, which were then rolled to 0·5-in.-thick plate (1) directly, (2) by cross rolling after direct rolling to a thickness of 1·3-in., or (3) by cross rolling. Specimens of these plates were subjected to different heat-treatment schedules and, finally, for each steel in each condition studied, Charpy V-notch specimens, taken both transverse and longitudinal to the main rolling direction and notched perpendicular to the plate surface, were broken at —320°, —150°, —40°, +80° and +300°F. (—195°, —100°, —40° +25° and + 150°C.).

Data illustrating the influence of the following factors are discussed: variation in sulphur content; cross rolling; hardness; tempering temperature; microstructure (pearlitic microstructures and those resulting from slack quenching were studied); homogenization treatment; melting stock (three of the steels were made from electrolytic iron, the remainder from a charge of ingot iron).

The authors consider that the data presented warrant the following conclusions:

'1. Increasing sulphur content in an alloy steel of the base composition studied decreases Charpy V-notch impact-resistance in a regular manner at hardness levels in the range R_c 25–40, for both straight- and cross-rolled conditions. Charpy values of these steels, when plotted on logarithmic co-ordinates, show a straight-line relationship to sulphur content.

'2. Sulphur content did not markedly affect the Charpy impact transition temperature of these steels, although there was a trend toward a moderate decrease in transition temperature with increasing sulphur content.

'3. Directionality in plates of the steel studied depends on rolling practice and not on sulphur content. Cross rolling decreases the spread in Charpy values between longitudinal and transverse specimens proportional to its amount and independent of sulphur content.

'4. The effect of sulphur on impact properties is similar in steels with pearlitic or slack-quenched microstructures to that in steels with tempered martensitic microstructures, for steels with sulphur contents of 0·06 per cent. or below.

'5. Notched-bar impact values are improved by an homogenization treatment of 10 hr. at 2350°F. (1285°C.), independent of sulphur content, but directionality of properties is relatively unaffected. This treatment results in a rounding of sulphide inclusions, which is believed to be the principal factor in the improved impact properties.'

Ballistic and Charpy-Impact Tests on Armour Steels

W. P. HATCH: 'Correlation of Toughness Between H-Plate and Charpy-Impact Test.'

Welding Jnl., 1960, vol. 39, Jan., pp. 20s-30s.

The laboratory work reported in the paper originated in ballistic tests on three types of armour steel: low-alloy manganese-molybdenum and nickel-chromium-molybdenum steels heat-treated to high-hardness for maximum resistance to penetration, and a low-alloy nickel-chromium steel heat-treated to a lower hardness for maximum resistance to shock. The data derived from the ballistic tests on H-plates indicated certain consistent differences between the three steels when welded with a given electrode. The most notable distinction was the marked tendency towards plate cracking exhibited by the high-hardness manganese-molybdenum-steel basis metal when welded by either ferritic or austenitic electrodes. In the case of the high-hardness nickel-chromium-molybdenum basis metal, no plate cracking was observed, but all five rounds fired caused excessive weld-joint cracking. In the low-hardness nickel-chromium steel, failure occurred also only in the weld joint. The laboratory tests were undertaken (1) to determine variations in the hardness, soundness and toughness of the basis metals, and (2) to investigate the feasibility of predicting, on the basis of Charpy-impact tests, the differences indicated by the ballistic tests.

The basis steels were subjected to chemical analysis, macro- and microexamination, hardness tests, and Charpy-impact tests. Charpy-impact tests were carried out also on welded specimens.

The relative performance of the high-hardness manganese-molybdenum and the low-hardness nickel-chromium steel test plates were found to be predictable from Charpy V-notch impact-transition curves. The manganese-molybdenum armour steel failed to meet minimum specification impact requirements for unwelded plate, while in the nickel-chromium plate the impact transition occurred entirely below —40°F. (—40°C.). In the case of the high-hardness nickel-chromium-molybdenum steel plate, the agreement between Charpy transition data and the performance as indicated by the ballistic tests on H-plate specimens was not so definite, although the transition temperatures of the nickel-chromium-molybdenum basis metal were slightly lower than those of the manganese-molybdenum armour steel.

Determination of Cobalt in Steels

See abstract on p. 63.

HEAT- AND CORROSION-RESISTING MATERIALS

Alloying Behaviour of the γ' phase

R. W. GUARD and J. H. WESTBROOK: 'Alloying Behaviour of Ni_3Al (γ' Phase).'

Trans. Metallurgical Soc., Amer. Inst. Mining, Metallurgical and Petroleum Engineers, 1959, vol. 215, Oct., pp. 807–14.

The excellent elevated-temperature strength exhibited by many nickel-base heat-resisting alloys is attributable to the presence of a dispersion of the Ni_3Al (γ') phase in a solid-solution matrix. In a recent investigation, WESTBROOK found that, although considerable intergranular brittleness was evident in a coarse-grained specimen of Ni_3Al arc-melted in an inert atmosphere, individual grains were readily deformable (see abstract in *Nickel Bulletin*, 1957, vol. 30, No. 10, p. 184). The same study showed also that Ni_3Al exhibited an anomalous temperature/hardness curve, characterized by a number of peaks, in the range room temperature to 800°C., which could not be correlated with any microscopically observable precipitation reactions or polymorphic transformations. It was therefore proposed, in the study described, to investigate the reasons for the anomalous strength behaviour at high temperatures, and to examine solid-solution alloying of the compound and the effects of such alloying on its hardness.

Ni_3Al specimens, and specimens of various solid solutions based on Ni_3Al, were prepared by arc-melting in an inert atmosphere and then homogenized by heat-treatment at 1275°C. Micro-indentation hardness tests were conducted *in vacuo* over the range room temperature to 800°C.: the hardness/temperature curves are presented in the paper.

The investigation comprised three phases. In the first, an attempt was made to explain (in terms of precipitation hardening, defect hardening, domain hardening, or strain ageing) the anomalous hardness/temperature curve exhibited by unalloyed Ni_3Al. In the second, an investigation was made of the extent and nature of the solid-solubility in Ni_3Al of the following elements: chromium, copper, titanium, cobalt, iron, manganese, molybdenum, silicon, vanadium and zirconium. In the third phase, the influence of solid-solution alloying on the hardness of Ni_3Al was studied. To this effect, alloys were prepared in most of the ternary systems reviewed in the second phase, the compositions being selected to lie along a line connecting the stoichiometric Ni_3Al phase with the point of maximum solubility.

From data derived in phase one of the study it is concluded that (1) strain ageing by the interstitials carbon, oxygen and nitrogen is probably responsible for the observed hardness peaks, and the location and magnitude of the peaks are dependent on the identity and amount of interstitial present. The authors' observations with respect to the findings of the other phases of the investigation are summarized as follows:

'Elements which dissolved substitutionally in Ni_3Al (interstitial solutes were not considered) can be divided into three groups: those which substitute for nickel (cobalt and copper); those which substitute for aluminium (silicon, titanium, manganese, and vanadium); and those which substitute for both constituent elements (iron, chromium and molybdenum).

'The present investigation has revealed a hitherto unsuspected aspect of the mechanical behaviour of Ni_3Al, namely strain aging. The presence of this phenomenon has in part confounded the observations on solid-solution hardening although certain conclusions seems clear:

'(1) Only silicon and titanium impart significant hardening at either room- or elevated temperatures.

'(2) As with terminal solid solutions, lattice strain plays a major rôle in solid-solution hardening of a compound.

'(3) Defect hardening (or softening at high temperature) can be of the same order of importance as solid-solution hardening.

'(4) Solid-solution hardening of compounds such as Ni_3Al is complicated relative to binary terminal solid solutions, due to the possibility of virtually independent substitution for component elements.'

See also

Study of the Compound Ni_3Al at High Temperatures

R. W. GUARD and J. H. WESTBROOK: 'Studies of the Compound Ni_3Al by High-Temperature X-Ray Methods.'

Ibid., pp. 871-2.

In 1953 KORNILOV and MINTS presented data on the thermal expansion and electrical conductivity of the compound Ni_3Al which indicated the possibility of a transformation in Ni_3Al at about 600°C. (see *Doklady Akad. Nauk*, S.S.S.R., 1953, vol. 88, pp. 829-32). The present note presents the results of some observations of the Debye-Scherrer patterns for Ni_3Al at 800° and 1000°C.

On the basis of the X-ray results, it is concluded that any transformation present does not involve disordering of the structure or any gross crystallographic change. Measurements of linear expansion revealed no discontinuity in expansion coefficient up to 1000°C. In addition, determination of the hardness of Ni_3Al as a function of temperature has revealed no discontinuous change in the hardness curve near 600°C. characteristic of a polymorphic transformation, but a peak in hardness was observed which appears to be caused by strain ageing due to oxygen in solution.

Secondary-Phase Reactions in γ'-Hardened Austenitic Alloys

W. C. HAGEL and H. J. BEATTIE: 'High-Temperature Aging Structures in γ'-Hardened Austenitic Alloys.'

Trans. Metallurgical Soc., Amer. Inst. Mining, Metallurgical and Petroleum Engineers, 1959, vol. 215, Dec., pp. 967-76.

In heat-resisting alloys, such as the nickel-base materials 'Udimet 500', 'Nimonic 80' and 'Inconel X', mechanisms for both cellular and general precipitation are operative during ageing. In this paper the authors present the findings of an investigation of the variables involved in the secondary-phase reactions occurring during solution- and ageing-treatment in alloys hardenable by precipitation of γ', i.e., 'Nimonic 80', 'Inconel X', 'Udimet 500', modified 'Udimet 500', a cobalt-nickel alloy, and a cobalt-nickel-iron alloy.

Variations in the phase reactions were determined as a function of solution-treatment in the range 1700°F-2200°F. (925°-1205°C.), and of ageing for times up to 1000 hr. in the range 1200°-1800°F. (650°-980°C.) after solution-treatment for 8 hours at 2100°F. (1150°C.). After heat-treatment the specimen was V-notched and its impact-resistance was determined at room temperature. One half of the fractured specimen was used to provide powder residues for X-ray analysis, while the other was ground on both sides for hardness testing. The ground half was finally sectioned preparatory to optical- and electron-microscopical examination.

The following conclusions are drawn from the data and photomicrographs included in the paper:

'(1) In chromium-bearing nickel-base alloys, $M_{23}C_6$-containing cells quickly precipitate on isothermal aging, and their growth ceases with the general precipitation of γ' in the adjacent matrix.

'(2) The form of γ' particles appears to be related to γ'/matrix lattice mismatch; if this exceeds about 1 per cent., as it does in cobalt-nickel alloys without chromium, γ'-containing cells grow to impingement.

'(3) $(Cr,Ni,Mo)_{23}C_6$ is stable up to about 2100°F. (1150°C.); $(Cr,Ni)_{23}C_6$ transforms to $(Cr,Ni)_7C_3$ above 1900°F. (1040°C.), unless low carbon content causes a decreased solution temperature.'

Precipitation Reactions in Nickel-Aluminium Alloys

R. O. WILLIAMS: 'Aging of Nickel-base Aluminium Alloys.'

Trans. Metallurgical Soc., Amer. Inst. Mining, Metallurgical and Petroleum Engineers, 1959, vol. 215, Dec., pp. 1026–32.

The investigation reported was undertaken to throw light on precipitation reactions in nickel-aluminium alloys.

The six alloys studied, which contained 4·0, 5·5, 7, 8, 13·3 and 14·2 per cent. of aluminium, respectively, and were produced by vacuum-melting and -casting, were homogenized, subjected to varying degrees of cold work, and then (in some cases after recrystallization treatment) aged at temperatures up to 1000°C. Information on the ageing process was obtained by determining variations in hardness and electrical resistivity as a function of temperature and time at temperature, and by microstructural examination using X-ray - diffraction and microscopical techniques.

The results are considered to justify the following conclusions:

'(1) The aging of nickel-rich aluminium alloys is caused by the precipitation of Ni_3Al in the form of coherent plates on the (100) planes. The strains necessary to provide this coherency are 0·7 per cent. or less.

'(2) The isothermal aging suggests that there are two consecutive processes. The first is believed to be a change of atomic configuration, presumably increasing short-range order; the second is the actual precipitation of Ni_3Al. For times greater than used here, or at higher temperatures, the particles will undergo competitive growth.

'(3) Discontinuous precipitation has also been observed and is shown to follow the idea of Smith in starting by the motion of existing grain boundaries. Nucleation inside the grains takes place when deformation has preceded the aging. It is believed that the precipitate which forms as a result of this process is always incoherent.

'(4) With the possible exception of the higher aluminium contents, precipitate particles do not lose coherency for those treatments used here. This included the resolution of the particles by raising the temperature. In agreement with this was the observation that the alloys did not overage in terms of hardness.

'(5) The experimental observations prove beyond reasonable doubt that the general precipitation was homogeneous. Calculations based on nucleation theory are in fair agreement. Additionally, there appears no problem in accounting for the particle size based on existing methods and data.

'(6) The application of the order-hardening theory, supplemented by a rough application of the theory of mechanical interaction, appears adequate to explain the observed strengths (as hardness).'

Influence of Silicon Additions on Friction and Wear of Nickel Alloys

D. H. BUCKLEY and R. L. JOHNSON: 'The Influence of Silicon Additions on Friction and Wear of Nickel Alloys at Temperatures to 1000°F.'

Amer. Soc. Lubrication Engineers, 1959, *Preprint* 59LC-11; 16 pp. + figs.

The literature contains numerous references to the improvements in the performance of bearing metals achieved by addition of small amounts of silicon. The increase in hardness which results from such additions, and which has been the subject of considerable investigation, cannot *per se* be the cause of this improvement, and attention has been directed to the possibility that the effects of silicon in this respect may be attributable to its inducing and supporting the formation of surface films. In the investigation reported by the authors an attempt was made to determine the validity of this hypothesis by tests on silicon-containing nickel-base alloys.

Six materials were selected for study: a nickel-chromium-iron alloy containing nickel 70, chromium 15, iron 5–9, per cent., and small amounts of silicon, carbon, manganese, sulphur, aluminium, titanium and niobium; low-carbon cast nickel (99·4 per cent. nickel); and four nickel-silicon alloys containing, respectively, 10, 7·5, 5·0 and 2·5 per cent. of silicon.

Friction and wear tests were carried out at temperatures in the range 75°–1000°F. (25°–540°C.), using the following environments: air, mixtures of oxygen and argon, a mixture of hydrogen and nitrogen, and a halogenated methane gas lubricant (CF_2Br_2). In all the sliding tests both disc and rider were fabricated from the same material. Friction, wear and hot-hardness data are presented, and details are given of the results of complementary metallographic studies and analyses of the surface films present.

These data confirm that the film-forming tendencies of silicon contribute greatly to the success of silicon-containing alloys as slider materials at elevated temperatures. Friction coefficients varied from 0·05 to >10·00, depending on film-formation characteristics. The formation of surface-reaction films in oxidizing atmospheres (containing oxygen or bromine) was found to be induced more readily with the silicon-containing nickel alloys, and the formation of such films was accelerated at elevated temperatures. The most satisfactory results were obtained with nickel-silicon alloys containing 5–10 per cent. of silicon (and having a duplex structure). Film formation occurred either by a surface-flow mechanism or by surface reactions. In the case of the duplex alloys, the surface flow of the softer α - phase (Si-Ni solid solution) over the harder β-phase (Ni_3Si) during sliding provided a beneficial surface film, and this mechanism was of predominant importance when the tests were carried out in a reducing atmosphere.

Influence of Silicon on High-Temperature Oxidation of Stainless Steels

J. F. RADAVICH: 'Effect of Silicon on High-Temperature Oxidation of Stainless Steels.'

Corrosion, 1959, vol. 15, Nov., pp. 613t-7t.

Work to determine the effects of composition on the oxidation-resistance of heat-resisting materials has involved study mainly of the influence of trace elements. The few experiments carried out to throw light on the rôle of trace elements in this respect have revealed that these elements influence oxide-film growth by modifying the conditions at the metal/oxide interface; in particular, the silicon content of ferritic steels seems to play an important part in increasing oxidation-resistance at high temperatures. The investigation now reported was conducted to obtain further information on the influence of silicon content on the oxidation behaviour of stainless steels.

The study was made on a series of 16-10-type chromium-nickel stainless steels having silicon contents of 0·17, 0·27, 0·42, 1·06, 1·71 and 3·55 per cent. Samples were oxidized for 5, 30 and 90 minutes at 600°C., and for 5 and 30 minutes at 800°C. In other tests specimens were oxidized for 10 hours at 1000°C. with the aim of correlating the growth of the oxide film and oxide-scale formation at this higher temperature. After oxidation the specimens exposed at 600° and 800°C. were examined by X-ray fluorescent analysis, electron microscopy, and electron-diffraction and X-ray-diffraction techniques. Oxide scales and sub-scales formed during oxidation at 1000°C. were studied optically in cross section, as well as by X-ray diffraction and fluorescent analysis.

The data presented are supplemented by photomicrographs of oxidized specimens.

The oxidation-resistance of the stainless steel was found to increase, and the amount of oxide nodules formed to decrease, rapidly with increase in silicon content, until, at a high silicon level (3·55 per cent.), a very thin oxide film formed at the lower temperatures, while at 1000°C. very little oxide scale was determined.

The mechanism underlying the oxidation-resistance conferred by the presence of silicon appears to be explicable in terms of the metal's influence in decreasing the number of defects in the initial oxide films formed at the metal/oxide interface. This decrease induces chromium enrichment at the metal/oxide interface and in the oxide films, and consequently the rate of diffusion of iron outward to form the oxide scale is greatly retarded.

Evaluation of the Oxidation-Resistance of Nickel-containing Alloys

J. SANNIER, R. DOMINGET and R. DARRAS: 'Oxidation in Air of Two Heat-Resisting Alloys ('Nicral D' and 'Hastelloy X') at 900° and 1100°C.'

Jnl. Nuclear Materials, 1959, vol. 1, Oct., pp. 213-25.

In the work reported the authors have attempted to determine the suitability and reliability of two methods of assessing, in preliminary screening tests, the relative oxidation-resistance of two or more heat-resisting materials: (1) using a thermobalance; and (2) by manual measurement of loss-in-weight after subjecting the oxidized specimens to an appropriate descaling treatment. These two techniques were supplemented by metallographic examination of sectioned samples after oxidation treatment.

The efficacy of the two methods was studied in relation to their application to two materials: the steel 'Nicral D'* and the alloy 'Hastelloy X'†. In the first phase of the programme the materials were oxidized in air at 900° and 1100°C., and variations in weight were continuously recorded by means of a thermobalance. The rate of oxidation of 'Nicral D' increased considerably between 900° and 1100°C.: on the basis of a 200-hour test, the rate had increased from $2{\cdot}2\times10^{-3}$ mg./cm.²/hr. at 900°C. to $1{\cdot}8\times10^{-2}$ mg./cm.²/hr. at 1100°C. At 900°C. the oxidation rates exhibited by the two materials were similar, but at 1100°C. 'Nicral D' was found to oxidize more rapidly than 'Hastelloy X'. On the other hand, metallographic examination revealed that after 150 hours' exposure at 1100°C. 'Nicral D' exhibited signs both of intergranular oxidation and a small amount of internal oxidation, whereas 'Hastelloy X' was found to be particularly susceptible to internal oxidation.

While, on the basis of the data obtained, the thermobalance is considered to be a convenient method of studying oxidation, its advantages are limited to tests on only one specimen at a time. In the remainder of the investigation the authors therefore compared two descaling methods which, in determining loss-in-weight, enable separation of the oxide without attack on the basis metal: the one, an electrolytic method involving use of a sodium-hydroxide/sodium-carbonate solution; the other, a chemical method involving exposure to a sodium-nitrate/sodium-peroxide solution. Tests in this connexion were made on specimens oxidized, cooled and weighed only once. The results presented show that, while both descaling methods are applicable to 'Hastelloy X', the chemical method does not appear suitable for use with 'Nicral D'.

The overall finding of the authors is that metallographic examination, used in conjunction with appropriate descaling techniques, offers an accurate means of studying the oxidation characteristics of high-temperature alloys.

The thermobalance should be reserved for relatively short tests or to act as a control over the other techniques employed.

Response of 'Inconel 700' to Heat-Treatment

J. R. MIHALISIN and J. S. IWANSKI: 'Microstructural Study of the Response of a Complex Superalloy to Heat-Treatment.'

Trans. Metallurgical Soc., Amer. Inst. Mining, Metallurgical and Petroleum Engineers, 1959, vol. 215, Dec., pp. 912-16.

Recent studies of commercial nickel-base high-temperature alloys have demonstrated the importance

	C	*Mn*	*Si*	*Ni*	*Cr*	*Fe*	*Mo*	*Ti*
* 'Nicral D'	0·05	0·63	1·56	17	21·73	59	—	—
† 'Hastelloy X'	0·04	0·76	0·71	48·09	21	17·3	8·20	0·23

of the morphology of carbide phases in relation to the properties of the alloy (see, for example, papers abstracted in *Nickel Bulletin*, 1957, vol. 30, No. 10, pp. 185–6, 129–30; 1959, vol. 32, No. 7, pp. 224–5). The purpose of the present study was to obtain information on the morphology and identity of the phases precipitated in 'Inconel 700' as a result of heat-treatment, and hence to correlate microstructure and heat-treatment.

The specimens studied were from hot-rolled bar of the following composition: cobalt 27·61, chromium 14·9, molybdenum 2·92, aluminium 2·85, titanium 2·22, iron 0·42, copper 0·02, carbon 0·1, silicon 0·12, manganese 0·07, per cent., remainder nickel. The influence of four heat-treatments was investigated:

(A) 2275°F. (1245°C.) for 2 hr. WQ

(B) 2275°F. (1245°C.) for 2 hr. WQ
+2000°F. (1095°C.) for 1 hr.

(C) 2275°F. (1245°C.) for 2 hr. WQ
+1600°F. (870°C.) for 48 hr.

(D) 2275°F. (1245°C.) for 2 hr. WQ
+2000°F. (1095°C.) for 1 hr.
+1600°F. (870°C.) for 48 hr.

Treatment (D) had been found to result in optimum stress-rupture life and ductility. Treatment (C), although producing a satisfactory response to ageing, resulted in low ductility. Treatments (A) and (B), representing component stages in treatments (C) and (D), were included to provide a basis of comparison in the microstructural studies.

Specimens in each condition of heat-treatment were subjected to optical- and electron-microscopical examination, which was supplemented by X-ray-diffraction analysis of electrolytically extracted residues. The authors' comments on the data obtained are quoted below.

'The preceding microstructural study of 'Inconel 700' shows that a solution and ageing treatment that results in impaired ductility can be associated with Widmanstätten precipitation of M_6C carbide at grain and twin boundaries. This type of precipitation can be suppressed by intermediate holding at a temperature between solution and ageing temperatures. This intermediate hold at 2000°F. (1095°C.) probably involves precipitation of titanium carbide, which either prevents M_6C carbide from precipitating, or restricts its formation to some more desirable distribution upon subsequent ageing at 1600°F. (870°C.). The precipitation of titanium nitrides and carbides randomly throughout the matrix may add to the strength of the alloy since they exist as a hard, dispersed phase. The age-hardening precipitate was identified as being of the γ' $Ni_3(Ti,Al)$ type and was ordered. Although the γ' phase is generally considered to be an ordered structure, very little attention has been given to the kinetics of the order-disorder phenomenon in this phase. The latter phenomenon is known to have a large effect upon physical properties, as studies on other systems have shown. Thus it may be significant that in a previous study, on 'Nimonic 80', no superlattice reflections were recorded for the γ' precipitate, although the same techniques were used as in this study. Of course, this could also be related to the higher titanium to aluminium ratio in 'Nimonic 80' as compared to 'Inconel 700'. This would have the effect of reducing the intensities of superlattice reflections in the γ' phase, because of its higher titanium content. Nevertheless, this order-disorder reaction may have an important effect upon strength in superalloys and deserves further study.'

Influence of Nitrogen and Manganese Contents on the Structure and High-Temperature Properties of Cast 'X-40' Alloy

E. E. FLETCHER and A. R. ELSEA: 'The Effects of Variations in Nitrogen and Manganese Content on the Structure and High-Temperature Properties of Cast 'X-40' Alloy.'

Trans. Metallurgical Soc., Amer. Inst. Mining, Metallurgical and Petroleum Engineers, 1959, vol. 215, Dec., pp. 917–25.

Although cast cobalt-base alloys such as 'X-40'* possess high strength at elevated temperatures, the scatter in the properties of different heats of the alloys is considerable. In this paper the authors give details of research conducted in an attempt to determine the factors contributing to this variation in properties and, if possible, to find ways of eliminating their effect. Earlier work having indicated that variations in the high-temperature strength of vacuum-melted 'X-40' alloy might be attributable to changes in the nitrogen or manganese content of the castings, an attempt was made in the present investigation to gain more information on the influence of these two elements.

Stress-rupture specimens, cast from vacuum-melted stock into which various percentages of nitrogen or manganese had been introduced, were subjected to stress-rupture tests at 1500°F. (815°C.) as a means of correlating structure and properties with variation in nitrogen and manganese content.

The results show that variations in nitrogen content had a pronounced influence on the high-temperature properties of the alloy. Specimens containing 0·01 per cent. of nitrogen (the lowest level studied) exhibited a 100-hour rupture-strength about equal to that of the commercial grade of alloy. Increases in the nitrogen content resulted in a progressive decrease in the rupture-strength, until, at a level of about 0·1–0·2 per cent. nitrogen, strength was at a minimum. This decrease could not be correlated with any change in microstructure, but when the nitrogen content was increased still further, the formation of progressively increasing amounts of a lamellar, pearlitic-type structure at the grain boundaries was associated with increases in rupture-strength. At nitrogen contents greater than about 0·25–0·33 per cent., the rupture-strength exceeded the normally reported values.

Two series of melts representing different melting stocks were found to exhibit minimum rupture strengths at different nitrogen contents, a finding which is considered to suggest that some unidentified

* Nominal composition: chromium 25, nickel 10, tungsten 8, iron 1·5, manganese 0·5, sulphur 0·5, carbon 0·05, per cent., remainder cobalt.

trace element not removed by vacuum-melting has a strong influence on the response of the alloy to variations in nitrogen content.

Of the series of specimens with manganese contents ranging from 0·6–3·2 per cent., that with the lowest manganese content exhibited the highest 100-hour rupture strength at 1500°F. (815°C.). Variations in manganese content had no appreciable effect on the microstructure.

Properties and Applications of 'René 41'

R. J. MORRIS: 'More Information on 'René 41' Nickel Alloy.'

Materials in Design Engineering, 1959, vol. 50, Nov., pp. 157, 158, 160, 162.

'René 41', an age-hardenable nickel-base high-temperature alloy developed by the General Electric Company, is now available in the U.S.A. in the form of sheet, bar, billet, and investment castings. In this short article notes are given on heat-treatment, properties and applications.

The alloy can be vacuum-melted either by induction or consumable-electrode melting techniques, and both methods are currently being employed to produce ingots weighing up to 3,000 lbs.

'René 41' first attracted attention as a possible light-weight substitute for heavy forgings in jet engines, but the alloy is considered suitable also for heat-resisting bolting and fasteners used in the airframe parts of high-speed aircraft. As shown in the table below, 'René 41' is a modification of the high-temperature alloy 'M-252':

Element	'M-252'	'René 41'
Carbon	0·10-0·20	0·12 max.
Cobalt	9·0-11·0	10·0-12·0
Molybdenum	9·0-10·5	9·0-10·5
Chromium	18·0-20·0	18·0-20·0
Titanium	2·25-2·75	3·0-3·3
Aluminium	0·75-1·25	1·4-1·8
Silicon	0·50 max.	0·50 max.
Manganese	0·50 max.	0·10 max.
Iron	5·0 max.	5·0 max.
Boron	0·003-0·010	0·003-0·010
Nickel	Balance	Balance

Data presented demonstrate that the yield strength of the modified alloy is significally higher, at both room and elevated temperatures, than that of 'M-252', and, on a strength/weight basis, the alloy is claimed to be superior to comparable high-temperature alloys in the temperature range 1000°–1800°F. (540°–980°C). The material can be satisfactorily formed and welded (filler materials include 'René 41' wire and sheared strip, and 'Hastelloy X' or 'Hastelloy W' wire). Heat-treatments developed for the alloy are briefly discussed.

See also

R. J. MORRIS: ' René 41' . . . New Higher-Strength Nickel-base Alloy.'
Metal Progress, 1959, vol. 76, Dec., pp. 67–70.

Copper-Nickel-Tantalum Heat-Resisting Alloys

C. S. SMITH: 'Alloys of Copper, Nickel and Tantalum.'
Trans. Metallurgical Soc., Amer. Inst. Mining, Metallurgical and Petroleum Engineers, 1959, vol. 215, Dec., pp. 905–9.

The investigation outlined by the author was conducted to establish the influence of tantalum additions on the properties of copper and copper base alloys.

The initial experiments showed the solubility of tantalum in pure molten copper to be 0·025 per cent. at about 1200°C. The tantalum additions completely deoxidized the metal (without seriously impairing electrical conductivity), and lowered the recrystallization temperature. Further studies on a wide range of copper-rich alloys established that tantalum exhibits significant solubility only in copper-nickel alloys. The copper-rich corner of the copper-nickel-tantalum constitution diagram was investigated and the solubility of tantalum was found to increase rapidly with nickel content: at nickel contents of 15, 20, 30 and 50 per cent., solubility at 1100°C. was about 0·6, 1·2, 2·7 and >9 per cent., respectively. Solubility decreased with temperature, and the alloys were shown to be precipitation-hardenable.

Preliminary studies of precipitation-hardenability were made on rolled strip which, both as-quenched from 1100°C. and after subsequent cold rolling to achieve a 50 per cent. reduction, was heat-treated for three hours at various temperatures in the range 500–900°C. Typical hardness data are presented. The greatest hardness was exhibited by an alloy containing about 30 per cent. nickel and 1·6–5 per cent. tantalum, but, provided the tantalum content exceeded 0·16 per cent., some age-hardening occurred even with a 10 per cent. nickel alloy. (A tantalum content of 0·35 per cent. was needed in the 15 and 20 per cent. nickel alloys, and more than 0·75 per cent. with those containing 30 per cent. nickel.) The maximum hardness was obtained by heat-treating the as-quenched specimens at 700–750°C. and the cold-worked at 650–700°C. The cold-worked alloys with 2 per cent. tantalum and 30 per cent. nickel exhibited no microscopically visible recrystallization after three hours at 800°C. (Beryllium-copper alloys attain maximum hardness after ageing at 275°C., and even the chromium-copper electrode alloys soften at temperatures above about 500°C.)

Data illustrating tensile and elevated-temperature properties are included in the paper. At 700°C. the tensile strength of the strongest alloy is almost twice that of the plain cupro-nickel, and at 550°C. is equal to that of the standard material at room temperature.

The following general observations are made:

'Copper-nickel-tantalum alloys made with commercial 'ferro-tantalum' had tensile properties slightly superior to those alloys made with pure tantalum. Niobium behaves much like tantalum and can be partially substituted for it. If carbon was present in the alloy, it formed insoluble tantalum carbide and anything above 0·04 per cent. was eliminated from the melt (unless zinc was present, in which case as much as 0·09 per cent. carbon was retained). Embrittlement due to precipitation of graphite was never observed on annealing.

'A large number of other elements, in amounts of 0·1 to 1 per cent., were added to a base 68–30–2 copper-nickel-tantalum alloy. These generally had little effect, which indicates that the alloy would be relatively insensitive to impurities in commercial production.

'The corrosion-resistance of many alloys was measured by alternate immersion in hydrochloric or sulphuric acids, in salt spray, and by local impingement by sea-salt solution. The behaviour of copper-nickel alloys was unchanged by the addition of tantalum alone, though the addition of tantalum plus 1 per cent. silicon conferred a very slightly improved resistance to acids. The resistance to scaling at 700°C. was also slightly superior in this alloy, although otherwise the alloys were indistinguishable in their oxidation-resistance from straight cupro-nickel.'

'Cufenloy 30': Copper-Nickel Alloy for Heat-Exchanger Tubes

'Copper-Nickel Alloy Usable at 850°–900°F.'

Materials in Design Engineering, 1959, vol. 50, Nov., pp. 177, 178, 180.

The article (which is based on a paper presented by W. F. SIMMONS, B. J. SIROIS, D. N. WILLIAMS and R. I. JAFFEE at the 62nd Annual Meeting of the American Society for Testing Materials) discusses data on the physical, mechanical and creep properties of the wrought 70–30 copper-nickel alloy 'Cufenloy 30'.* The alloy, developed by Phelps Dodge Copper Products Corporation, Philadelphia, as a material of construction for heat-exchanger tubes, is deemed, on the basis of the data discussed, to possess the strength, ductility and resistance to stress corrosion necessary for service in unfired pressure vessels at temperatures up to 850°–900°F. (455°–480°C.).

The test programme outlined was initiated to obtain data which, superseding those (chiefly creep data) previously serving as design criteria for annealed copper-nickel condenser tubes, would enable full advantage to be taken of the higher mechanical properties offered by 'Cufenloy 30'.

Attention is directed to *Case No.* 1266 (*Special Ruling*), issued by the Boiler and Pressure Vessel Committee of the American Society of Mechanical Engineers, approving maximum permissible stresses for 'Cufenloy 30' at temperatures up to 800°F. (425°C.). The ruling specifies a minimum tensile strength of 72,000 p.s.i. (32 t.s.i.: 50·5 kg./mm.²), a minimum yield strength of 50,000 p.s.i. (22 t.s.i.: 35 kg./mm.²), and a minimum elongation of 20 per cent. At 750° and 800°F. (400° and 425°C.) the maximum permissible stresses are, respectively, 14,400 and 8000 p.s.i. (6·5 and 3·5 t.s.i.; 10 and 5·5 kg./mm.²): a graph indicating other stress maxima is included in the article. Other properties covered by the ruling conform to *A.S.T.M. Specification B*-111 for copper and copper-alloy seamless condenser tubes and ferrule stock.

* Nominal composition: copper 70, nickel 29·1, iron 0·5, manganese 0·35, per cent.

Creep of Cold-Drawn Nickel

See abstract on p. 41.

Use of Nickel-containing Alloys for High-Temperature Strain Gauges

R. BERTODO: 'Development of High-Temperature Strain Gauges.

Instn. Mechanical Engineers, 1959, *Preprint* 35/38; 14 pp.

The investigation outlined in the paper was initiated in 1953 in an attempt to evolve a successful high-temperature strain gauge which would contribute to the development of high-power axial turbojets and rocket motors of advanced design. The basic requirement was for a gauge capable of recording alternating strain data to an accuracy of about ±5 per cent. at temperatures up to 1000°C., mainly in tests on turbine blades under operational conditions. A further prerequisite was that the life of the gauge should be sufficient to permit readings to be obtained at stress levels in excess of ±10 tons/sq. in. (22,500 p.s.i.: 15·5 kg./mm.²) on 'Nimonic' alloys. To achieve this aim a suitable bonding agent capable of withstanding the high scrubbing velocities involved was also necessary.

In the initial stage of the programme long unbonded wires, fabricated from the following materials, were tested in tension at room temperature: 'O nickel'; 'Nichrome'; 'Brightray C'; 'Nimonic 90'; 'Karma 331'; soft iron; piano wire; 'Nilo 42'; 'Tophet C'; 26 per cent. chromium-iron; 'Ni-Span C'; 'Advance'; 'Eureka'; 'Ferry; 'Monel'; 'Manganin'; 'Minalpha'; phosphor-bronze; platinum-iridium alloy.

With the exception of the piano wire and certain of those made from 'Brightray C' (which were evaluated in the hard condition), all the wires were annealed before testing. Sensitivity factors and resistivity were determined, and, on the basis of the results obtained (which are presented and discussed), fully-annealed wires in the following materials were subjected, this time in the form of gauges, to further evaluation at high temperature: 'Karma 31', 'Brightray C', 'Nimonic 90', 26 per cent. chromium-iron, and 'Eureka'. This evaluation involved studies of the influence, on the behaviour of the gauges, of such factors as metallurgical changes, geometry, and long-time exposure

at temperature. Typical failures of gauges incorporating the techniques evolved are discussed.

Work was also conducted on a number of bonding media, some commercially available, to obtain information on creep-resistance, shear-strength, and resistance to erosion and thermal shock.

In connexion with work on measurement of steady strains at high temperatures, temperature-compensation tests were carried out on specimens of 'Eureka', 'Brightray C' and 'Karma 331'.

It is concluded that the gauge factor is a function of the lattice imperfections of the element wire, and, as such, will be temperature-conscious only if the imperfections themselves are influenced by variations in temperature. In general, any factor affecting the resistivity will affect the sensitivity. Such phenomena as stress-relief and precipitation will influence the sensitivity to various degrees; a marked resistivity change is generally indicative of strain-sensitivity variations. In the case of nickel-chromium-alloy wires, the sensitivity factor will remain stable and predictable to ± 5 per cent., provided that the wires are cycled beyond the precipitation temperature and are operated below about 1050°C., and that certain precautions are observed during gauge manufacture and investment. The results suggest that these findings apply also to the cupro-nickel and nickel-chromium-iron alloys, though in this case the critical temperatures are induced by other equally well-defined factors.

A large number of bonding materials were proved unsuitable for high temperature operation (notably, vitreous compositions and silicate adhesives). Some ceramic cements are considered suitable, but these generally exhibit porosity and low insulation resistance at temperature, and are liable to spall if subjected to thermal shock after flame impingement. Both reducing and strongly oxidizing conditions are likely causes of bond failure.

Future requirements will, it is anticipated, be met by gauges manufactured by vacuum deposition of suitable alloys on to a pre-coat of desired shape.

Elevated-Temperature Properties of Niobium-containing Stainless-Steel Weld Metals

T. J. MOORE: 'Elevated-Temperature Properties of Modified Type 347 Weld Metals.'

Welding Jnl., 1959, vol. 38, Dec., pp. 457s-74s.

The work described formed the last phase of a comprehensive investigation undertaken in an attempt to determine a modification, or modifications, of Type 347 (18-8-Nb) weld metal which would be resistant to weld cracking, suitable for corrosion-resisting, high-temperature or low-temperature applications, and not subject to serious embrittlement at elevated temperatures. In the initial phases of the investigation (references to previous work are given in the paper) tests confirmed that weld-metal cracking is a function of ferrite content, and that the embrittlement of the niobium-bearing steels after exposure at elevated temperatures is due to transformation of ferrite to sigma. When ferrite was eliminated, however, cracking became a serious problem unless (as in compositions C and H of the present study) the carbon or the manganese content was substantially increased: even with such modification, the fully-austenitic welds were more susceptible to cracking than the partially-ferritic welds.

The present report is concerned with an evaluation of the elevated-temperature properties of the five compositions noted below (full details of compositions and of test procedures and conditions are included in the paper):

(A) 19-9-Nb (7 per cent. ferrite; Type 347);

(C) 19-13-Nb (0·12 per cent. carbon; fully-austenitic; modified Type 347);

(F) 19-10-LC (4 per cent. ferrite; Type 308 L);

(H) 19-13-Mn-Nb (5 per cent. manganese; fully-austenitic; modified Type 347);
16Cr-8Ni-2Mo (4 per cent. ferrite; modified Type 316).

The test programme comprised three phases: (1) Tensile tests, at temperatures in the range 1000°-2000°F. (540°-1095°C.), on as-welded all-weld-metal specimens; (2) Stress-rupture tests at 1000°, 1200° and 1300°F. (540°, 650° and 705°C.) on (A), (C), (F) and (H) all-weld-metal specimens, and transverse stress-rupture tests on niobium-bearing weldments, in the as-welded condition, after annealing, or after long-time exposure at temperature; (3) R.P.I. hot-ductility tests, in which weld metal was subjected, in equipment developed by the Rensselaer Polytechnic Institute, to thermal cycles equivalent to those encountered in the vicinity of an arc weld. Specimens in all three phases were submitted to metallographic examination after testing.

The conclusions drawn from the extensive data presented in the report are summarized as follows:

'(1) From a stress-rupture strength standpoint for temperatures between 1000 and 1300°F. (540° and 705°C.) the standard Type 347 (containing 7 per cent. ferrite), the high-manganese 347 or the high-carbon 347 electrodes would be more than adequate to join Type 347 stainless steel, since any of these weld metals are stronger than the base material. Stress-rupture tests, which were conducted on transverse specimens which had been aged for 10,000 hr. prior to testing, gave further evidence that these welds were stronger than Type 347 base plate, even after this prolonged ageing period.

'(2) Annealing generally improves the rupture ductility of the niobium-bearing welds, particularly at 1200° (650°C. and 1300°F.), without seriously reducing the stress-rupture strength.

'(3) The 308L weld metal, containing 4 per cent. ferrite, is weaker than Type 304L base material in both the as-welded and aged conditions.

'(4) The standard 347 weld, containing 7 per cent. ferrite, possesses inherently low tensile-ductility between 1500° and 2000°F. (815°-1095°C.) when loaded at strain rates which are conventionally

employed in elevated-temperature tensile tests, and its strength is above that of Type 347 base material. Thus, in annealing heavy sections, it is recommended that the heating rate to the annealing temperature be rapid from 1100° to 1925°F. (595° to 1050°C.) in order to minimize the chance of obtaining heat-affected-zone cracking in the base material.

'(5) For improved tensile ductility at elevated temperatures, as exhibited in conventional tensile tests, the high-manganese 347, 18-8-2, or, to a lesser extent, the high-carbon 347, would be an improvement over the standard partially-ferritic Type 347 electrode.

'(6) The good ductilities shown in the R.P.I. hot-ductility test for the partially-ferritic Type 347 and 308L welds confirm the fact that these weld metals have good resistance to hot cracking.

'(7) In the R.P.I. hot-ductility test, the high-carbon and high-manganese 347 compositions did not behave well, since these welds were slow to recover ductility on cooling from 2400° and 2450°F. (1315° and 1340°C.). On the other hand, these fully-austenitic weld metals had previously been given a relatively good rating in various cracking tests, although they were never as completely free from microfissuring tendencies as are the partially ferritic welds. Thus, granted that the fully-austenitic high-manganese and high-carbon welds are not completely free from microfissuring tendencies, these compositions have improved tensile ductility and superior stress-rupture strength to the standard partially-ferritic Type 347 weld metal, and are therefore logical choices for applications where good stress-rupture strength is required.

'(8) For the welding of heavy sections of Type 347 stainless steel the 16-8-2 electrode would have an advantage over the niobium-bearing welds, since its tensile strength is below that of Type 347 base material and it possesses relatively good ductility at 1800°-2000°F. (980°-1095°C.). This would assure that minimum heat-affected-zone stress concentrations would occur during welding and annealing. On the other hand, there is some laboratory evidence that, in service, the superior ductility of 16-8-2 weld metal in Type 347 pipe welds may cause stress concentrations to arise. The 16-8-2 electrode is not recommended for use in applications where intergranular corrosion-resistance is a service requirement.'

Corrosion of Aluminium-Nickel-Iron Alloys in High-Temperature Water

E. C. W. PERRYMAN: 'Aluminium Alloys for Water-Cooled Power Reactors.'

Jnl. Inst. Metals, 1959, vol. 88, Oct., pp. 62-73.

'Zircaloy 2', a zirconium-base alloy containing small additions of chromium, nickel and iron, possesses the high corrosion-resistance in high-temperature water and the low thermal-neutron cross-section necessary for use as a material for fuel sheathing in nuclear-power reactors. The alloy is, however, much more expensive than aluminium-nickel-iron alloys which (by virtue of their nickel and iron contents) are resistant to blistering and intergranular attack in high-temperature water, and which, like 'Zircaloy 2', have a satisfactory thermal-neutron cross-section. The purpose of the paper is to review data available on the corrosion-resistance and mechanical properties of the most satisfactory of the aluminium-nickel-iron alloys so far developed, and then, on the basis of these data and taking into account economic considerations, to assess their suitability for reactor service relative to that of 'Zircaloy 2'.

In the experiments discussed various aluminium-nickel-iron alloys, (some of which contained minor alloying additions) were subjected to static and dynamic corrosion tests in high-temperature water (including heavy water). The influence of heat flux, alloying additions and inhibitors was also taken into account, and, in addition to the corrosion data presented, the paper contains information on stress-rupture properties and fabrication and welding characteristics.

The aluminium-nickel-iron alloys studied exhibited corrosion rates in static high-temperature water which were very high relative to those of 'Zircaloy 2', but very low in relation to those of other commercial aluminium alloys. In high-temperature water flowing at 20 ft./sec. (6 m./sec.) the corrosion rate was considerably higher than that in static water, and it appears that little improvement can be anticipated from compositional modifications. The results suggest the necessity, in reactor applications, of using, in association with a low pH, some inhibitor such as phosphoric acid or silica, a procedure, which, it is considered, would then render the coolant incompatible with mild steel in other parts of the cooling system. The possibility exists that pre-filming may lead to a sufficiently low corrosion rate, but further investigation of this factor is needed. For use in conjunction with uranium-oxide fuel at reasonable power ratings, an aluminium-alloy sheath would have to be considerably thicker than one fabricated from 'Zircaloy', and this fact, together with the decrease in price of 'Zircaloy' tubing, is considered to render the aluminium-nickel-iron alloys, at the present stage of their development, economically unattractive for water-cooled power reactors.

See also following abstracts.

Corrosion of Nickel-containing Aluminium Alloys in High-Pressure Steam

N. J. M. WILKINS and J. N. WANKLYN: 'The Corrosion of Aluminium and its Alloys in High-Pressure Steam.'

Jnl. Inst. Metals, 1959, vol. 88, Nov., pp. 134-40.

Aluminium has been widely used as a material of construction for low-temperature nuclear reactors, but its use in pressurized-water reactors operating at temperatures higher than 150°C. is precluded by its poor corrosion-resistance under such conditions. A considerable amount of work has therefore been

carried out to develop resistant alloys, and much interest has been shown in the aluminium–nickel–iron alloys. In view of the growing interest in boiling-water reactors and in schemes involving steam cooling and nuclear superheating, it was deemed of technical importance to extend the study of the corrosion mechanism of these alloys to that obtaining in superheated steam at various pressures. Work carried out in this connexion at the A.E.R.E., Harwell, is described in the present paper.

Four materials were selected for study: the aluminium-base alloy 'Aereal 1' (containing nickel 2·59, iron 0·43, silicon 0·1, wt. per cent.); S.A.P. (containing about 10 per cent. oxide); a nickel/S.A.P. tube material (containing nickel 1, Al_2O_3 10, per cent.); and high-purity aluminium (included to enable study of the change in corrosion product from alumina to böhmite).

The specimens were exposed, in autoclaves, to steam at temperatures in the range 270°–500°C., in some cases for times in excess of 400 hours, but mainly for 24–, 48– or 96–hour periods. Full particulars of the test procedures and results are given in the paper. The authors' summary of their conclusions is quoted below.

'(1) At 325°C. the reaction of 'Aereal 1' (aluminium with 2·5 wt. per cent. nickel and 0·4 wt. per cent. iron) with superheated steam follows a parabolic relationship with time up to at least seven days. The weight gain at constant time is proportional to the fourth power of the steam pressure, and, at high pressures, approaches, without apparent discontinuity, values previously found in saturated steam.

'(2) A few experiments suggest that, at a given pressure, the actual corrosion of 'Aereal 1' decreases with increasing temperature between 270° and 350°C., and also that the pressure-dependence of corrosion is less at both 270° and 350°C. than at 325°C.

'(3) At 400° and 500°C. most 'Aereal 1' specimens are more or less completely destroyed by rapid penetrating attack. At 400°C. this takes the form of severe localized attack spreading from random starting points, but at 500°C. rapid, uniform growth and embrittlement of the whole specimen occurs. The few specimens which, at both temperatures, escape such attack, form thin protective films and corrode at a very low rate.

'(4) At 500°C. specimens of S.A.P. (Sintered Aluminium Powder) are significantly less liable to intergranular attack than 'Aereal 1'. They are, however, very rapidly attacked at 325° or 270°C.

'(5) The addition of 1 wt. per cent. nickel to S.A.P. appears, from preliminary tests, to give a material combining the good corrosion-resistance of 'Aereal 1' at temperatures up to 350°C. with the resistance of S.A.P. to penetrating attack up to 500°C.

'From the practical viewpoint this seems the most promising material, but longer tests, including stress specimens, are required.'

Localized Corrosion of Aluminium-Nickel Alloys in High-Temperature Steam

C. F. BRITTON and N. J. M. WILKINS: 'Localized Penetrating Corrosion of a Sintered Aluminium Powder Alloy in High-Temperature Steam.'

Jnl. Nuclear Materials, 1959, vol. 1, Dec., pp. 374–6.

This letter outlines the scope and salient findings of experiments carried out to determine the factors involved in the localized penetrating attack to which aluminium-nickel alloys have been shown to be subject in superheated steam.

Specimens of a S.A.P. alloy (containing oxide 6·5, nickel 0·75, iron 0·75, silicon 0·07, wt. per cent.) were exposed in steam at 400°C. and 1500 p.s.i. Omission of pickling prior to testing was found to increase the proportion of specimens attacked and, in an effort to determine the causes of this phenomenon, further tests were conducted to evaluate the effects of cold working, stress, coupling to stainless steel and to iron, surface contamination with $NiAl_3$ particles, and cathodic discharge of hydrogen before testing. Test conditions were varied to assess the influence of pressure, condensation, presence of air, and addition of hydrogen to the steam.

The results show that the penetrating attack was stimulated only when hydrogen was added to the steam environment. Experiments are now in progress to determine the metallurgical factors which will contribute to the resistance of such alloys under conditions which the experiments described have shown to be conducive to penetrating attack.

Suitability of Aluminium-Nickel Alloys for Reactor Service

J. B. COTTON: 'Aluminium Alloys for Water-Cooled Reactors.'

Nuclear Power, 1959, vol. 4, Oct., pp. 100–2.

In this paper the author assesses, in the light of work reported in the literature, the feasibility of developing aluminium alloys exhibiting the corrosion-resistance necessary for use in water-cooled reactors.

Discussion of the improvements in corrosion-resistance achieved by alloying additions (which is concerned mainly with the influence of nickel) is followed by a section indicating the corrosion behaviour of nickel-containing aluminium alloys subjected to dynamic-flow conditions. Reference is made also to research suggesting the possibility of using inhibitors to suppress corrosion under flow conditions.

In discussing the alloys so far developed, the author emphasizes that no full-scale commercial reactor in which all the fuel elements are canned with aluminium alloys is as yet operating with water or steam at temperatures higher than 200°C. In the U.S.S.R. fuel elements canned with an alloy containing silicon 9, nickel 1, per cent., have, however, been exposed for nine months in a water-cooled reactor at 275°C. and were in excellent condition when removed. Draley *et al.* report that, in the experimental reactor Borax IV, fuel elements sheathed in an aluminium alloy (containing nickel 1, iron 0·5, silicon 0·1–0·3, copper 0·1,

per cent.) have operated at 217°C. over a period of 300 megawatt days, and that, in the reactor at Argonne, plates of this alloy exhibited satisfactory corrosion-resistance after 15 months' exposure, during which the reactor produced steam at 250°C.

Residual-Oil-Ash Corrosion: Literature Review

C. J. SLUNDER: 'The Residual Oil Ash Corrosion Problem.'

Corrosion, 1959, vol. 15, Nov., pp. 601t-6t.

Although residual fuel oils have been used for many years in a variety of heating applications, corrosion by the products of combustion became an urgent problem only with the advent, after the war, of oil-burning steam boilers and gas-turbines operating at temperatures higher than 1100°F. (595°C.).

In this review of the subject, which is based on a *bibliography* of 57 items, the literature is critically surveyed in sections relating to general aspects of oil-ash corrosion, attempts to establish the mechanism of corrosion, work to evaluate the resistance of high-temperature alloys and to develop suitably resistant materials, use and development of protective coatings, and use of oil additives.

The following comments are considered justified in the light of the review:

'There is ample evidence that corrosion is caused by the vanadium, sodium and sulphur that occur in the ash. Compounds of low melting point are formed during the course of the combustion reaction, or perhaps by reactions taking place following combustion. These compounds appear to have strong fluxing action when molten, and in some manner act as oxygen carriers which result in accelerated corrosion at the metal/oxide interface. Economical procedures for removal of these elements have not been found.

'Many testing procedures have been used to evaluate the behaviour of heat-resistant alloys in these corrosive environments. While quantitative comparisons cannot be made, there appears to be general agreement that none of the presently-known alloys would have an acceptable service life under the conditions existing in boilers and gas-turbines burning residual oils. Nevertheless, some alloys are more resistant than others, and encouraging results have been obtained with some experimental alloys. Alloying additions such as silicon and aluminium are beneficial in this respect. The improved performance of experimental alloys indicates that the possibilities for a satisfactory solution to the problem may become more attractive as progress is made in the development of high-temperature alloys.

'Experiences with protective coatings also have been discouraging. While certain coatings appeared to have fair inherent corrosion-resistance, they have failed by cracking and undermining. Here also the possibility of obtaining improved coatings with beneficial elements concentrated in the outer surface layer of the metal is still open.

'The study of oil additives has received the greatest amount of attention. The approach is straightforward and the objective has been to add materials to the oil which react with the harmful components to form compounds which are solid at operating temperatures. Calcium, magnesium, aluminium and silicon compounds are most effective. Additives appear to have specific effects, that is, they do not provide equal protective effects for all variations of impurities, operating conditions and materials of construction.'

Corrosion of Nickel-containing Materials in a Hydrocarbon Conversion System

F. A. PRANGE: 'Corrosion in a Hydrocarbon Conversion System.'*

Corrosion, 1959, vol. 15, Dec., pp. 619t-21t; disc., p. 621t.

The paper is concerned with an exploration of the factors involved in the corrosion of steels and alloys used in butane-dehydrogenation equipment at the Plains Plant of Phillips Petroleum Company. The butane is dehydrogenated to butene, at 1100°F. (595°C.), over a chromia-alumina catalyst contained in tubes welded into groups (called 'harps'). Use of an unsuitable material for, or carburization of, the tube causes metal loss which contaminates the catalyst with red oxide dust. The dust is very catalytic, induces destructive cracking of the butane, and the considerable amount of carbon so formed results in rapid plugging of the system. The 27 per cent. chromium steel initially used for the 'harps' was selected on the basis of pilot-plant tests which indicated that it would not cause plugging. Exposure to the operating conditions, however, induced formation of sigma phase and the tubes became embrittled. Laboratory studies and plant tests were therefore initiated with a view to determining materials of construction more suitable for the tubing and other components of the system. By way of indicating the factors involved in the corrosion of the dehydrogenation equipment, the author gives details of these tests in the present paper.

Laboratory screening tests were carried out on iron, 'Duriron', nickel, and on straight-chromium and chromium-nickel stainless steels varying widely in alloying content. On the basis of these results, plant tests were conducted on tubing fabricated from Types 302B, 304, 310, 316, 321 and 347 chromium-nickel steels. Of these tubes, only those made from Types 302B, 310 and 316 (i.e., of 18-12-Si, 25-20 and 16-13-Mo type) did not plug, and carbon formation was excessively high with the molybdenum-bearing grade. After further tests it was decided to fabricate the catalyst tubes from Type 310 steel and the headers from Type 302B.

Findings with respect to the corrosion behaviour of the materials studied serve, in conjunction with the results of tests on 'Inconel' specimens, as a basis for discussion of possible corrosion mechanisms. Oxidation phenomena alone are not the governing factor, and the author tentatively suggests that the corrosion might be explicable in terms of the formation of a very unstable vapour-phase compound.

*One of three papers on metal dusting presented at the Fifteenth Annual Conference of the National Association of Corrosion Engineers.

Resistance of Nickel-containing Materials to Corrosion by Synthesis Gas from Methane/Oxygen Combustion

F. EBERLE and R. D. WYLIE: 'Attack on Metals by Synthesis Gas from Methane-Oxygen Combustion.'*
Corrosion, 1959, vol. 15, Dec., pp. 622t-26t; disc., p. 626t.

The investigation described originated in the discovery that severe metal wastage had occurred in uncooled gas-deflection baffles, soot-blower elements and other components fabricated from niobium-stabilized 18-8 (A.I.S.I. Type 347) and 25-20 (Type 310) chromium-nickel stainless steels after only three weeks' exposure to hot 'synthesis' gas in the waste-heat boiler of a synthesis-gas reactor.

The gas, consisting predominantly of carbon monoxide and hydrogen, was produced, for fuel synthesis of the Fischer-Tropsch type, by burning methane with oxygen. (Details of the construction of the waste-heat boiler and the location of the relevant components are given in the paper.) Metallographic examination of the affected parts gave rise to the following findings:

'In the highest temperature zone (1700°F. (925°C.) and possibly higher), i.e., at the level of the lowest baffles, the attack consisted predominantly of straight oxidation, which progressed in an intercrystalline manner with the formation of a semi-scale. Corrosion in this zone was not significant.

'As temperatures decreased to 1500°F. (815°C.) and lower, pitting corrosion set in, apparently initiated by localized carburization which was again followed by oxidation or decarburization.

'With further decrease in temperature down toward 1400°F. (760°C.), carburization seemed to get the upper hand. In this predominantly-carburizing zone the attack was only slight. However, here also were sporadic occurrences of alternating carburization and decarburization.

'At still lower temperatures, down to about 1100°F. (595°C.), cycling carburization and decarburization became the predominant phenomenon.'

In an attempt to find materials exhibiting higher resistance to this type of attack, specimens of the following types of alloy and steel were exposed in the unit at each centre-baffle location: carbon steel, chromium-molybdenum high-temperature steels, ferritic straight-chromium steels, chromium-nickel austenitic steels (Types 304, 304L, 347, 310), copper, aluminium-bronze, 'Armco 17-14 CuMo', 'Inconel', 'Monel', nickel, aluminized 'Inconel', various ceramic-coated or aluminized austenitic steels, and various pack-calorized specimens. Evaluation of the data presented on the loss-in-weight of these specimens showed that the materials suffering least attack were those most resistant to carburization (i.e., nickel, 'Monel', 'Inconel', 27 per cent chromium steel, copper, and pack-calorized stainless steel). Further tests, involving up to 25 days' exposure to the relevant operational conditions, confirmed these findings: 'Monel' and 'Inconel', in particular, were subject only to slight intergranular attack.

Cyclic carburization and oxidation or cyclic oxidation and reduction are suggested as the most likely fundamental processes involved in the wastage phenomenon.

*One of three papers on metal dusting presented at the Fifteenth Annual Conference of the National Association of Corrosion Engineers.

Deterioration of Stainless Steel in Atmospheres Containing Carbon Monoxide and Hydrogen

W. B. HOYT and R. H. CAUGHEY: 'High-Temperature Metal Deterioration in Atmospheres Containing Carbon Monoxide and Hydrogen.'*
Corrosion, 1959, vol. 15, Dec., pp. 627t-30t.

The paper gives details of an unusual type of deterioration encountered in equipment (fabricated from carbon steel or 25-20 Type 310 stainless steel) subjected to temperatures in the range 800°-1200°F. (425°-650°C.) in a plant producing gasoline from coal by the 'Synthol' process. Metal loss occurred by a process which, though as yet not fully understood, does not appear to be capable of interpretation in terms of chemical attack or erosion.

Metal deterioration was observed first (after about 3000 hours' operation) in the primary preheater and then, after about one year's further operation, in the secondary preheater of the reforming unit in which gas is prepared for synthesis reaction to form gasoline and related hydrocarbons. The gas mixtures by which the steel was attacked consisted mainly of hydrogen, carbon monoxide, steam and methane, with small percentages of carbon dioxide, nitrogen and heavier hydrocarbons (i.e., constituents which, taken singly, are known to be non-corrosive at the relevant temperatures and pressures).

Metallographic examination of affected components revealed that the deterioration had taken the form of pitting and general metal loss, without formation of adherent scale but accompanied by carburization of the attacked surface. Photomicrographs illustrating the deterioration are included in the paper, and the authors offer a tentative theory in explanation of the mechanism involved.

Calcination of Aqueous Radioactive Wastes: Corrosion Studies of Nickel-containing Materials

E. J. TUTHILL and R. F. DOMISH: 'Calcining Aqueous Radioactive Wastes.'
Industrial and Engineering Chemistry, 1959, vol. 51, Dec., pp. 1471-4.

Calcination of the radioactive waste solutions resulting from processing spent zirconium-uranium fuel elements offers an effective means of preparing them for safe disposal. Unfortunately, however, the calcination of the zirconium and aluminium salts contained in the wastes involves the formation of mixtures of gases which are highly corrosive. The study now reported was undertaken to determine the most suitable alloys for use as materials of construction in calciners processing such wastes.

The materials studied were exposed in rotary kilns during calcination of simulated aluminium-zirconium waste solutions. When steam is added, pyrohydrolysis of the zirconium fluoride present proceeds satisfactorily at 700°C., with evolution of hydrogen fluoride. The aluminium nitrate present is, however, convertible at 325°C. to the largely amorphous oxide, with evolution of nitrogen oxides. Since the mixture of gases formed during calcination in a single vessel was believed to be very corrosive, this temperature difference enabled an attempt to be made at separating the nitrogen oxides from the hydrogen fluoride by using two kilns in series, the first operating at 325°C. for denitration, and the second at 700°C. for defluorination. Corrosion tests were therefore conducted both in single- and double-kiln calciners.

In general, the specimens (machined to an accuracy of $\pm 0{\cdot}0001$ in.: 0·0025 mm.) were of shell-and-core type; the core, which was not subjected to the corrosive conditions, serving as a standard for determination of corrosion rate and depth of penetration. Specimens were exposed for 500 hours under conditions almost identical with those of a commercial plant Full details are given of the procedures and equipment used.

The materials evaluated included various grades of chromium-nickel and straight-chromium stainless steels 'Inconel X', 'Illium G', 'Ni-O-Nel', 'Haynes 25', 'Carpenter 20', 'Duranickel', 'Hastelloy C', 'Incoloy 804', 'Incoloy', '17-4 P.H.', 'S Nickel', 'Worthite', 'Hastelloy B', 'Inconel', 'Croloy 5', 'Monel', low-carbon nickel, high-tensile bronze, 'Ampco 16' and mild steel. Corrosion rates and maximum penetration are listed for each.

Attempts to separate the gases using the two-kiln system were unsuccessful, and corrosion rates were lower in the single-kiln calciner for nearly all the specimens tested. The materials with high nickel and chromium contents appeared to be the most corrosion-resistant, and at least four alloys are probably suitable for use in single- or double-kiln calciners: 'Illium G', 'Inconel X', 'Haynes 25' and 'Ni-O-Nel'.

Corrosion of Stainless Steels in Fuming Nitric Acid

M. L.-J. BERNARD: 'Corrosion of Stainless Steels in Fuming Nitric Acid.'

Corrosion et Anticorrosion, 1959, vol. 7, Nov., pp. 373–83.

Concentrated fuming nitric acid is assuming an increasingly important rôle in many fields of industry. The investigation described was undertaken to determine its corrosive effect on the conventional corrosion-resisting materials of construction, i.e., the various grades of stainless steel.

Nineteen stainless steels were tested: two were martensitic, two were ferritic, and the remainder austenitic. With the exception of one, a chromium-manganese-nickel steel, the austenitic grades were mainly of 18-8, 18-10, 18-12-Mo, 18-14-Mo, 25-15 and 25-20 type. Also included in the investigation were three alloys of 38-18, 77-20 and 80-20 nickel-chromium type.

The specimens were exposed to acid of the following composition: $HNO_3 \geqslant 98{\cdot}5$, $N_2O_4 \leqslant 0{\cdot}5$, $Al_2O_3 + Fe_2O_3 \leqslant 0{\cdot}01$, $H_2SO_4 \leqslant 0{\cdot}05$, per cent. The tests were carried out at two temperatures: at room temperature, and at the boiling point of the acid. In the room-temperature tests loss-in-weight was determined after one week, four weeks and eight weeks; loss-in-weight of specimens exposed to the boiling acid was established after one hour's exposure. The corrosion rates were studied as a function of the type of steel tested; of the time, temperature and pressure of the test; and of the pickling treatment to which the specimen was subjected. Full details are given of the data obtained.

The following general conclusions are drawn with respect to the behaviour of the different groups of material evaluated:

Martensic: Unsatisfactory resistance, principally in the boiling acid.

Ferritic: Good performance in the cold acid, relatively good in the boiling.

Austenitic:

(*a*) When the steel contained no titanium its performance was governed by its carbon content. At carbon contents less than 0·05 per cent., corrosion-resistance was good, even in the boiling acid.

(*b*) Stabilization with titanium improved the performance of the steel and resistance was good at both temperatures.

(*c*) The ferritic structure conferred by the presence of molybdenum or tungsten in some of the steels appeared to have a beneficial effect on corrosion-resistance. The performance of these steels was good in both tests.

(*d*) The good resistance exhibited by the alloy of 35-20 type was not reproduced in the two of higher nickel content.

These findings were for rolled steels: drawn specimens were, in general, more susceptible to corrosion. Investigation of the effects of conventional pickling treatments showed that corrosion-resistance did not vary significantly with the type of treatment employed.

At both test temperatures there was an initial period (one day at room temperature; ¼-hour at boiling point) in which virtually no corrosion occurred; this period was followed by a period of accelerated corrosion (a few days; ½-hour) associated with dissolution of the products of corrosion. Study of the corrosion data for both tests showed that corrosion rates at 86°C. were of the order of 100–200 times higher than those obtained at room temperature.

The paper ends with a survey of the types of corrosion to which the steels were subject. In the most resistant of the steels studied, corrosion was of general type. Use of the titanium-stabilized grades when welding is involved is, however, not recommended, due to risk of 'knife-line' attack.

It is shown that, properly heat-treated, the austenitic steels are not susceptible to stress corrosion in nitric acid. Galvanic-corrosion tests in nitric acid indicate the feasibility of conferring cathodic protection on austenitic steels by coupling them with aluminium or tin.

Determination of Cobalt in Nickel Alloys and Steels

K. L. CHENG and F. J. WARMUTH: 'Photometric Determination of Cobalt in Nickel Alloys and Steels.'

Chemist-Analyst, 1959, vol. 48, Dec., pp. 96–7.

Small amounts of cobalt present in nickel and other alloys are usually determined photometrically with 1-nitroso-2-naphthol, after volatilization of chromium as chromyl chloride and precipitation of other interfering metals with zinc oxide. The method is, however, tedious. A highly selective method for determination of small amounts of cobalt, based on the purple colour produced by nitrilotriacetic acid (NTA) and perborate, has been reported by Cheng. The colour reaction is specific under the conditions employed, and, if nickel and other metals are present, an excess of NTA is added to complex them. Since, however, the complexes of nickel, iron(III) and chromium are strongly coloured, and, since, moreover, NTA complexes of nickel, iron(III) and certain other metals are decomposed, with precipitation of NTA, upon addition of acid, it is deemed better to separate the cobalt from such metals if they are present in large amounts. The separation can be effected conveniently by anion exchange, and in the technique described in the paper anion-exchange separation precedes determination of small amounts of cobalt in nickel alloys and steels by the NTA-perborate colorimetric method.

The technique is considered suitable for determination of cobalt in amounts up to 0·5–5 mg., and it is noted that the anion-exchange separation can be omitted if the basis metals in a given alloy do not yield a very intense colour.

Cracking of Welded Chromium-Nickel Austenitic Steels: Literature Survey

J. C. BORLAND and R. N. YOUNGER: 'Some Aspects of Cracking in Welded Austenitic Steels: A Survey of the Literature.'

British Welding Jnl., 1960, vol. 7, Jan., pp. 22–59.

Report B5/1/59 of the British Welding Research Association.

Provided that the correct practices and procedures are employed, the welding of the austenitic chromium-nickel stainless steels normally offers little difficulty. Special precautions must be taken to prevent the occurrence of hot cracking and porosity in welding the free-machining grades (A.I.S.I. Type 303), in which, as in the high-silicon steels (Types 302B and 314), dilution is an important factor to be considered. In severely restrained sections the stabilized grades (Types 321 and 347) are susceptible to cracking in the heat-affected zone. Cracking (either of the weld or basis metal) can occur during welding, stress-relief treatment, or service. In the present paper, 'the considerable literature on this subject has been reviewed, and conclusions have been drawn which may help to provide a better understanding of the basic mechanisms—metallurgical and mechanical—causing cracking in these steels'.

The literature (the survey is based on a *bibliography* of 162 items ranging in date of publication from before 1948 to 1959) is collated in sections concerned with the following aspects of the subject: the constitution of the chromium-nickel austenitic steels; nature and incidence of cracking; factors affecting weld-metal cracking, i.e., pre-heating, delta ferrite, chemical composition (the influence of sulphur, phosphorus, carbon and silicon, niobium, manganese, molybdenum, copper, vanadium, zirconium, hydrogen, oxygen, nitrogen), post-weld heat-treatment, strength and ductility of the weld metal at high temperatures, sigma formation; factors affecting basis-metal cracking (incidence of cracking, methods of evaluating susceptibility to cracking, effects of cold-working and grain-size, effect of alloying additions and delta ferrite, stress-rupture measurements); theories of weld-metal cracking; and theories of basis-metal cracking.

The scope of the survey is extremely comprehensive, and the information reviewed is supplemented throughout by references to numerous tables, curves and diagrams.

The conclusions to which the survey gives rise are summarized as follows:

Weld Metal

'Weld-metal cracks which occur during welding of the fully austenitic materials are probably, in most instances, due to the presence of small quantities of liquid residing at the grain boundaries while the weld is solidifying and, at the same time, being subjected to moderate or excessive strain.

'Elements which are extremely harmful, even when present in very small amounts (less than 0·1 per cent.), are sulphur and phosphorus. Less harmful elements, but which still demand careful control, are carbon, silicon, niobium, zirconium, copper and vanadium.

'If these harmful elements are present in relatively large quantities, then the probability of cracking is reduced because of the reduced strains developed, the beneficial effect of grain refinement, and the fact that the increased quantity of liquid (eutectic) acts as a filler. Thus, in a eutectiferous system, cracking reaches a maximum at the maximum extent of the brittle range and, thereafter, decreases. Weld metal of near-eutectic composition is ideal from the weldability viewpoint.

'The presence of 5–10 per cent. ferrite in the weld structure (austenitic/ferritic alloy) prevents cracking; smaller quantities will frequently prove effective. Its beneficial action is probably due to its capacity for dissolving larger quantities of harmful elements (like phosphorus, silicon, and niobium) than can austenite, and to its action in creating an increased grain-boundary area, which thins out the liquid films and also lessens the tendency to segregation. The Parks' hypothesis that ferrite acts to concentrate the ferrite formers and cause liquation demands further study before it can be accepted.

'High-temperature brittleness is another factor which has been proposed as a cause of cracking, but it seems likely that, because of the limited temperature range in which it is found, this low-ductility region

(about 1000°C.) would not be troublesome. This factor is probably important in post-weld heat-treatment or in service, or both.

Base Metal

'Base-metal cracks not connected to the fusion line are probably due to the presence of liquid films of lower melting point than the bulk material. Liquid healing is unable to take place. Although the liquid films cannot be modified in character by additions to the weld pool (e.g., ferritizers), cracking may be reduced by altering the composition of the weld metal to decrease the strain. It should be possible to deposit weld metal which is coherent only at a temperature lower than the solidus of the base metal, and thereby reduce the strains imposed upon the base metal during its liquid-film stage. Equally well, a weld metal with lower plastic resistance than that of the base metal (e.g., 16Cr-8Ni-2Mo on 18Cr-12Ni-1Nb steel) should be beneficial, since the strains on the base metal should be lessened.

'Fusion-line cracks can be started by low-melting-point segregates in the base metal and, once formed, can, under favourable circumstances, propagate into the weld metal.

'Fusion-line cracks may also be caused by the Rehbinder-Medovar effect (grain-boundary penetration). In this case cracking may be reduced by modifying the composition of the weld pool. Copper appears to be the element which is most harmful in this respect.

'High-temperature brittleness has also been proposed as a cause of cracking, but supporting evidence is lacking.

Cracks formed after Welding

'It is not clear from the literature whether the initiation of service failures takes place during welding, during stress relief, or during service.

'It has been suggested that the properties of the heat-affected zone are unimpaired by the welding cycle, and that cracking is due to the high stress levels existing in the weldment.

'This suggestion is, however, not universally accepted and requires further study.'

Intergranular Corrosion-Resistance of Welded Nickel-Molybdenum-base Alloys

G. N. FLINT: 'The Corrosion-Resistance of Welded Nickel-Molybdenum Alloys.'

HENRY WIGGIN AND CO. LTD., *Publn.* 1735*.

Reprint from *Jnl. Inst. Metals*, 1959, vol. 87, May, pp. 303-10: see abstract in *Nickel Bulletin*, 1959, vol. 32, No. 7, pp. 233-4.

The work described has resulted in the production, on a commercial scale, of a wrought nickel-molybdenum-iron-vanadium alloy of closely controlled composition, which, marketed under the Registered Trade Mark 'Corronel 220', is available in most mill forms. That the alloy is substantially free from susceptibility to weld decay has been proved by extensive field trials under conditions in which the conventional nickel-molybdenum alloys have failed prematurely due to weld decay.

Developments in Brazing Nickel-Base High-Temperature Alloys

E. H. KINELSKI and J. B. ADAMEC: 'New Developments in Brazing High-Temperature Nickel-Base Alloys.'

Welding Jnl., 1959, vol. 38, Dec., pp. 482s-6s.

The investigation reported was undertaken in an attempt to satisfy the need for a brazing procedure, or a brazing alloy, capable of producing sound high-strength joints in nickel-base high-temperature alloys. The authors were concerned with both approaches to the problem: in one phase, work was carried out on the development of a brazing alloy which would be self-fluxing in an inert-gas atmosphere, 'non-aggressive' to the basis metal, and exhibit good flow and wettability at a brazing temperature below 2250°F. (1230°C.); in the other phase, the authors investigated the feasibility of improving the performance of commercial brazing alloys by pre-placing nickel powder on the surfaces to be joined.

To provide a basis for evaluation of the experimental brazing alloys studied, 'Inconel-X' plug-and-cylinder specimens, brazed under production conditions using various commercial brazing alloys, were subjected to tensile-shear tests at 1200°F. (650°C.) and to stress-rupture tests at 1200°F. and 1500°F. (815°C.). Some of the specimens were nickel plated before brazing; others were brazed using borax flux. The highest shear-strength (41,100 p.s.i.; 18·5 t.s.i.; 29 kg./mm.^{2}) was obtained using a nickel-chromium-boron brazing alloy and borax flux in a dried-hydrogen atmosphere. Stress-to-rupture tests on similar shear joints gave the following strengths for a 100-hour life: (*a*) 1200°F., 27,000 p.s.i.; (*b*) 1500°F., 6500 p.s.i.

Tee-joint specimens of 'Inconel X', 'Inconel 700', 'Incoloy 901' and 'Inconel 713C' were employed to assess the flow and wettability characteristics of the experimental alloys. These experiments, and tensile and stress-rupture tests on brazed 'Inconel X' specimens, showed that best results were obtained with a 60-40-type palladium-nickel alloy containing small amounts of lithium and boron. The advantages of this alloy are summarized as follows:

'(1) Good wettability and excellent capillary-flow and fillet-forming characteristics.

'(2) No aggressive penetration into base metal and no formation of brittle intermetallic compounds.

'(3) A brazing temperature of 2150°F. (1175°C.).

'(4) No need for a flux for furnace brazing in an argon atmosphere.

'(5) High shear strength at 1200° F.(650°C.). 'Inconel X' age-hardenable nickel-chromium alloy brazed with this alloy exhibited an average strength of 30,550 p.s.i. (13·5 t.s.i.; 21·5 kg./mm.^{2}) in shear in short-time tests.

'(6) Preliminary stress-to-rupture test results on shear joints in 'Inconel X' brazed with this alloy were as follows for a 100-hour life: (*a*) 1200 F., 18,000 p.s.i.; (*b*) 1500°F., 3000 p.s.i.'

* *We shall be pleased to supply a free copy of this publication.*

Although the temperature strength of the specimens brazed with the commercial alloys were high in comparison with those obtained with the new palladium-nickel self-fluxing alloys, the need for flux, the aggressive penetration of the brazing alloy into the basis metal, and the brittleness of the joint are disadvantages not exhibited by joints obtained with the new alloys.

Pre-placing nickel powder (in the form of a slurry with an acrylic-resin binder) on 'Inconel X', 'Inconel 700', 'Incoloy 901' and 'Inconel 713C' facilitated the flow of brazing alloys in joints brazed in an argon atmosphere. Tensile-shear tests at 1200°F. (650°C.), on 'Inconel X' brazed with pre-placed carbonyl-nickel powder and a nickel-chromium-boron brazing alloy, showed the specimens to have an average shear strength of 31,400 p.s.i. (14 t.s.i.; 22 kg./mm.²).

Thermal Fatigue of Brazed Components

R. L. PEASLEE: 'Thermal Fatigue and High-Temperature Brazements.'

Welding Jnl., 1960, vol. 39, Jan., pp. 29-33.

With the advent of the jet engine, and the direct exposure to the gas stream of thin-section components of fabricated parts (e.g., vanes, nozzles, liners, etc.), the aeronautical engineer has been confronted with one more cause of failure, that of thermal fatigue. Brazing is a process often used to join very thin sheet metal to heavier sections, a type of assembly which is subject to thermal fatigue when cyclically heated at high temperatures. In this article the author first outlines the characteristic features of thermal-fatigue failure, and subsequently, in discussing case histories of such failure, illustrates the causes and effects of, and the precautions to be taken against, thermal fatigue in brazed parts. Discussed in this connexion are failures in brazed turbine stator blades, rocket-engine parts, heat-exchanger components, and honeycomb structures. Examples of thermal fatigue in industrial applications are also considered.

ANALYSIS

Determination of Nickel in Zirconium

See abstract on p. 44.

Determination of Cobalt in Nickel Alloys and Steels

See abstract on p. 63.

Corrigenda

Nickel Bulletin, 1960, vol. 33, No. 1-2.

Properties and Applications of '17-4 P.H.' Steel, pp. 19-20, last paragraph, first line.

For '17-7 P.H.' *read* '17-4 P.H.'

Corrosion of Nickel and 'Inconel' in a Fused-Salt Environment, p. 28.

For W. D. MANLY *read* D. H. JANSEN.

For U.S. Atomic Energy Commission, Report ORNL 57-6-72, 1959; 8 pp.,

read U.S. Atomic Energy Commission, Report ORNL 57-6-72, 1957; 8 pp.

Attention is drawn to the fact that many of the names of materials mentioned in The Nickel Bulletin are *Registered Trade Marks*.

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